The removal of colour from textile dye using biosorbent

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Abstract
The basic dye acid blue 9 (AB 9) adsorption performance of low-cost adsorbent, tamarind seed, was studied. AB9 adsorbent removal efficiency was studied as a function of various adsorption parameters such as temperature, adsorbent dosage, contact time, adsorbent size and agitation intensity which were optimized for removal of AB9 from the aqueous medium using Response Surface (RSM) process.

The significance of various adsorption parameters along with their combined effect on the adsorption process was identified through a complete factor design of 50.

Keywords*:* Optimization, Biosorbent, Textile dye, Tamarind seed, Acid blue 9(AB9).

Introduction

Industrialization and urbanization are the two causes of chemical agents that induce deterioration of the environment. They quickly played a beneficial and detrimental environmental role. Most companies such as colouring, textiles, paper and plastics use dyes to colour their products and often require huge quantities of water. Consequently, they contain huge volumes of colored runoff. It is recognised that color significantly affects the understanding of water quality by the general public. Colour is the first contaminant found in wastewater. The first contaminant to be found in wastewater is color[1]. Rather small amounts of dyes are highly visible and unacceptable in water (less than 1 ppm for some dyes)[2].

There are more than one lakh commercially available colours and more than seven lakhs tones are produced annually[3]. Synthetic dyes are common water pollutants because of their good solubility and they can often be found in trace quantities in industrial wastewater.

An indication of the scale of the problem is the fact that 2% of the dyes produced are discharged directly into aqueous effluent. Dyes have a significant effect on aquatic photosynthetic activity and reduced light penetration and may also be harmful to some aquatic life due to the presence of aromatics, metals or chlorides[4-6]. Dye wastewater is usually treated by physical or chemical or biological treatment processes. Due to strict restrictions on the organic content of industrial effluents, dyes must be separated from the wastewater prior to discharge. Many of these colors are also toxic and cancerous, posing a serious risk to marine living organisms[7].

Dye wastewater is usually treated through physical- or chemical or biological treatment processes. These include chemical coagulation/flocculation, ozonation, oxidation, ion exchange, irradiation, precipitation and adsorption[8]. Some of these techniques have proved to be effective, even though they have limitations. These include: excess chemical use or accumulation of concentrated sludge with obvious disposal problems, expensive plant or operational costs, lack of effective colour reduction and sensitivity to variable inputs of wastewater.

Various physical methods such as membrane filtration processes (nanofiltration, reverse osmosis, electro dialysis) and adsorption techniques are also commonly used.The main drawback of membrane processes is that they have a limited lifespan before membrane fouling occurs and therefore the cost of periodic replacement must be included in any economic viability study. Liquid-phase adsorption provides an attractive alternative for the treatment of contaminated water[9,10], Adsorption is a well known balancing mechanism and an effective method for water decontamination applications[11,12].

Adsorption has been found to be superior to other water reuse strategies in terms of initial cost, design versatility and usability, ease of use and insensitivity to toxic pollutants. Adsorption also does not contribute to the production of harmful substances.

Activated carbon is quite expensive[13]. Both chemical and thermal recycling of spent carbon is expensive, practically on a large scale, resulting in excessive effluent and a significant loss of adsorbent. This has led many researchers to explore the use of cheap and efficient

alternative materials such as wood, fly ash, palm fruit bunch, rice husk, peat, activated clay, bagasse pits, cassava peel, palm tree cobs, dats, fruits, stones, nutshells, *Hydrilla verticillata* and *Turbinaria conoides*[14-18]. The aim of this work is to investigate the adsorption capacity of acid blue 9 from aqueous solutions by using tamarind seed as an adsorbent, a material that is very low-priced and readily available in most countries.

Material and Methods

Preparation of solution with aqueous dye: By dissolving 1 gram of deionized water with acid blue 9 in 1 litre, stock solution was prepared. Diluting the stock solution AB9 supplies the remaining necessary concentrations. Fresh dilutions are used for each trial. The pH of the operating solutions is matched to ideal values with hydrochloric acid or sodium hydroxide. In the literature the dyes structure and properties are given[18].

Preparation and Properties of sorbent: Tamarind seeds come from tamarind indica fruits. To extract the seed hull, it was soaked overnight in water and washed double with double distilled water to remove lighter resolvable materials. It was then dried in the oven at 70^{0}C for one hour. It was then crushed with mortar and pistol and then separated to varying mesh sizes. The literature offers the physicochemical properties of Tamarind seed[19].

Experimental design by Response surface methodology (RSM)

Design of experiment (DOE): The RSM has number of design groups with their individual properties and functions. The most common designs used by researchers are central composite design (CCD), Box–Behnken design and three-level factorial design. CCD was used to study the effects of the variables on their reactions and subsequently in optimization studies.[19] This approach is ideal for fitting a quadratic surface and allows with a minimum number of experiments to refine the effective parameters as well as to evaluate the interaction between the parameters. In order to assess whether there is a relationship between the factors and the response variables examined, the data collected must be studied using regression in a statistical manner.

A regression design is usually used to model a response as a mathematical (known or empirical) function of few continuous factors and to expect good model parameter estimates[20]. Batch experiments were conducted on the basis of central composite design to explain the effects of temperature, adsorbent dosage, contact time, particle size and agitation velocity on the percentage removal of Acid blue 9 dye.

$$x_i = \frac{X_i - X_o}{\Delta x}$$

where x_i is coded value of the ith variable, X_i is uncoded value of the ith test variable and X_0 is uncoded value of the ith test variable at center point. The range and levels of individual variables are given in table 1. The experimental design is given in table 2 along with experimental data and predicted responses. The regression analysis was performed to estimate the response function as a second order polynomial:

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i X_i + \sum_{i=1}^{k}\beta_{ii} X_i^2 + \sum_{i=1, i<j}^{k-1} \sum_{j=2}^{k}\beta_{ij} X_i X_j$$

where Y is the predicted response, β_i, β_j, β_{ij} are coefficients estimated from regression. They represent the linear, quadratic and cross products of x_1, x_2, x_3 on response.

A statistical program package Design Expert 7.1.5 was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation. The equations were validated by the statistical tests called the ANOVA analysis.

Experimental procedure: Adsorption of acid blue 9 from aqueous solution to tamarind seed was performed under shaking conditions in an orbital shaker (REMI-12, India). The experiments were carried out in accordance with the central composite design. A necessary quantity of tamarind seed has been added to each in 100mL Acid Blue 9 in 250 mL of Erlenmeyer flask. The mixture was agitated in an incubated orbital shaker at the desired temperature and speed for the time intervals specified. At 4000 rpm, the supernatant was separated by centrifugation for 10 mins. The residual concentration of the supernatant was estimated. UV-Vis (Elico, SL 164, Hyderabad, India) spectrophotometer assessed the dye concentration in the raw and treated specimen.

The analyses were performed at a wavelength of 619nm in a UV-Vis Spectrophotometer. The calibration plot for acid blue 9 was drawn between percentage absorbance and standard dye solutions of varying strengths. The concentration of the treated dye sample was determined from the observed absorbance value of the initial concentration. The response the removal efficiency of acid blue 9 was calculated as follows:

$$Y(\%) = \frac{(C_o - C_i)}{C_o} \times 100$$

where Co, Ci are the initial and final concentration of the dye solution. All experiments have been conducted in triplicate and mean values have been reported. Maximum deviation was found to be ±3%.

Table 1
Levels of different process variables in coded and un-coded form for adsorption of Acid blue 9

Variable	Code	-2.38	-1	0	+1	+2.38
Temperature, ^{o}C	A	20	30	40	50	60
Sorbent dosage, g	B	0.1	0.2	0.3	0.4	0.5
Contact time, min	C	100	150	200	250	300
Particle size, mm	D	0.35	0.246	0.17	0.124	0.074
Stirring Speed, rpm	E	100	150	200	250	300

Table 2
Experimental conditions and observed response values of 2^5 Central Composite Design

Run. No	A- Temperature	B- Sorbent dosage	C- Contact time	D- Particle size	D- Stirring Speed	Percentage Colour removal	
						Experimental	Theoretical
1	-1	-1	1	-1	1	58.3	54.62
2	-1	1	1	1	-1	48.0	40.56
3	-1	1	-1	1	1	93.2	93.55
4	0	0	0	0	0	87.0	86.93
5	1	-1	-1	1	1	49.0	41.37
6	1	1	1	1	1	60.0	65.47
7	0	0	0	-2.37841	0	52.0	56.96
8	1	1	1	-1	1	67.0	69.72
9	1	1	-1	-1	1	69.0	64.98
10	0	0	0	0	0	87.0	86.93
11	0	0	0	0	0	60.0	63.41
12	1	1	-1	1	1	50.2	56.23
13	-1	1	-1	1	-1	87.0	86.93
14	0	0	0	0	0	64.0	56.48
15	1	1	-1	-1	-1	35.8	26.78
16	2.37841	0	0	0	0	87.0	86.93
17	0	0	0	0	0	43.3	48.95
18	1	1	-1	1	-1	55.9	48.32
19	1	-1	1	-1	1	61.2	68.83
20	0	2.37841	0	0	0	59.0	58.69
21	1	1	1	-1	-1	69.0	70.79
22	-1	-1	-1	-1	1	35.0	37.70
23	1	-1	1	1	1	52.0	57.44
24	1	-1	-1	-1	-1	35.0	33.49
25	-1	1	1	-1	-1	68.0	66.42
26	-1	1	1	1	1	79.0	73.47
27	-1	-1	-1	1	-1	79.0	70.07
28	-1	-1	-1	-1	-1	45.0	52.06
29	-1	-1	1	1	-1	30.8	37.34
30	1	-1	1	1	-1	50.0	51.36
31	-1	-1	1	-1	-1	30.6	24.82
32	0	0	0	0	-2.37841	47.9	53.92
33	1	-1	1	-1	-1	87.0	86.93
34	0	0	0	0	0	87.0	86.93
35	0	0	0	0	0	39.8	46.67
36	-1	1	-1	-1	-1	87.0	86.93
37	0	0	0	0	0	72.6	63.87
38	0	-2.37841	0	0	0	38.0	43.55
39	1	-1	-1	1	-1	35.0	42.92
40	-2.37841	0	0	0	0	41.2	45.89
41	0	0	0	0	2.37841	62.0	61.29
42	-1	-1	1	1	1	55.0	53.39
43	-1	1	1	-1	1	87.0	86.93
44	0	0	0	0	0	78.0	77.81
45	0	0	-2.37841	0	0	70.3	80.15
46	-1	-1	-1	1	1	73.0	63.83
47	-1	1	-1	-1	1	62.0	55.94
48	0	0	0	2.37841	0	39.0	49.31
49	1	-1	-1	-1	1	52.0	48.48
50	0	0	0	0	0	58.9	57.99

The process variables temperature, adsorbent dosage, contact time, particle size and agitation speed were optimized and the pH effect and initial dye concentration were studied under these optimized conditions.

Results and Discussion

Optimization of process parameters for acid blue 9 dye sorption with Tamarind seed

Experimental design and fitting for a quadratic model: The second order of the polynomial eq. 5 represents a mathematical model for the reduction of the percentage of color with independent process variables. The results are analyzed by using ANOVA and are shown in table 3. The Model F-value of 13.42 indicates that the model is significant. It is found from the P values that among the test variables used in the study, A, C, E, AB, AD, BE, A^2, B^2, C^2, E^2 are significant model terms.

The expected R^2 of 0.6302 is in sensible agreement by the adjusted R^2 of 0.8353. The appropriate of the model is too expressed by the regression coefficient R^2, which is found to be 0.9050, representing that 90.50 % of the response variability could be explained by the model. This means that the forecast of experimental data is relatively satisfactory.

The magnitude of coefficients in table 3 shows the maximum positive contribution of adsorbent dosage and agitation speed on the percentage dye removal whereas the contact time, adsorbent size and temperature have a negative effect on the removal of percentage colour. The quadratic temperature conditions, adsorbent dosage, contact time, adsorbent scale and agitation velocity have a negative effect on color removal.

Further, the interactions of 'temperature and adsorbent dosage', 'temperature and contact time', 'adsorbent dosage and contact time', 'adsorbent dosage and particle size', adsorbent dosage and agitation speed have positive effect whereas the interactions of 'temperature and agitation speed', 'contact time and agitation speed', 'adsorbent dosage and contact time', 'adsorbent dosage and particle size' and 'contact time and particle size' have negative effect on percentage colour removal.

Response surface estimation for maximum removal of acid blue 9 using Tamarind seed: Five process variables were used to test their effect on the sorption process using the surface response technique. The response surface methodology was used to investigate the interactive effect of two factors on the percentage of dye and the three-dimensional plot was drawn. The interaction effects and optimal levels of the variables were determined by diagramming the surface curves.

The surface curves of a 3D response are shown in figs. 1–10. Illustration 1 is the interactive effect of temperature and sorbent dose on removal of AB9 dye. The response surface curves shape shows good interaction between those variables tested. The combined effect of temperature and contact time on removal of AB9 dye is shown in fig. 2. By fig. 2 the efficiency of the removal was expected to increase with the adsorbent dose. The average percentage of color removal is 83 percent at a given 35^0C temperature range and 2.7 g / L level of sorbent dose. The optimum value of both variables i.e. temperature and adsorbent dosage can be calculated by load point or by checking the X and Y coordinate limits.

Fig. 3 depicts the interaction of temperature and agitation speed, where the highest color removal percentage of 76 per cent was found to occur at 35^0C and 215 rpm agitation. The combined effect of temperature and particle size was shown in the form of 3D plot in fig. 4.

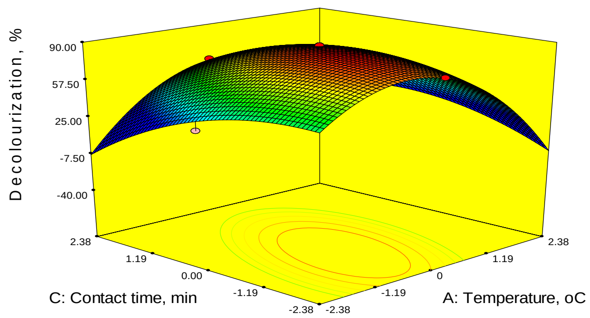

Figure 1: Response surface plot of the combined effects of temperature and sorbent dosage on the percentage colour removal of acid blue 9 by tamarind seed

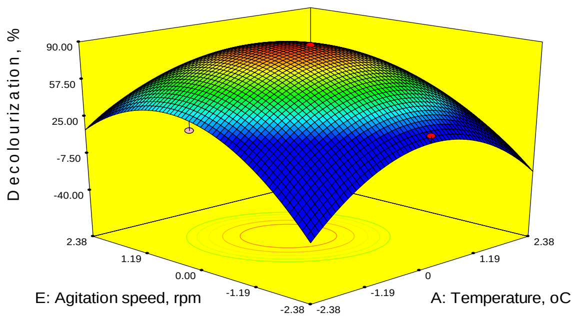

Figure 2: Response surface plot of the combined effects of temperature and contact time on the percentage colour removal of acid blue 9 by tamarind seed

Fig. 5 expresses the impact of sorbent dosing and contact time on the biosorption percentage of AB9 dye. From the figure it was found that at the sorbent dose 2.7g / l, the maximum biosorption occurs when the contact time is 249 min, which is according to the model. The shape of the contour shows good interaction between the sorbent dosage and contact time, which is clearly illustrated in fig. 5. The combined effect of sorbent dosage and particle size was shown in the form of 3D plot in fig. 6.

Table 3
Analysis of Variance (ANOVA) for Response Surface Quadratic Model

Source	Coefficient factor	Sum of square	DF	Mean square	F	P>F
Model	86.91	14145.97	20	707.30	13.42	< 0.0001
A	-3.39	498.88	1	498.88	9.47	0.0045
B	1.04	47.14	1	47.14	0.89	0.3521
C	-4.16	750.76	1	750.76	14.25	0.0007
D	-0.22	2.00	1	2.00	0.038	0.8468
E	4.43	850.31	1	850.31	16.14	0.0004
A*A	-9.2	4705.91	1	4705.01	89.30	< 0.0001
B*B	-3.63	733.85	1	733.85	13.93	0.0008
C*C	-3.36	627.36	1	627.36	11.91	0.0017
D*D	-5.38	1610.88	1	1610.88	30.57	< 0.0001
E*E	-9.11	4615.95	1	4615.95	87.59	< 0.0001
A*B	5.56	1024.91	1	1024.91	19.45	0.0001
A*C	3.80	461.32	1	461.32	8.75	0.0061
A*D	-4.32	597.72	1	597.72	11.34	0.0022
A*E	-2.22	157.09	1	157.09	2.98	0.0949
B*C	1.43	65.84	1	65.84	1.25	0.2728
B*D	1.59	80.96	1	80.96	1.54	0.2251
B*E	4.16	553.61	1	553.61	10.51	0.0030
C*D	-0.67	14.45	1	14.45	0.27	0.6046
C*E	0.63	12.88	1	12.88	0.24	0.6248
D*E	1.49	71.10	1	71.10	1.35	0.2549
Residual		1528.21	29	52.70		
Lack		1528.21	22	69.46		
Fit		0.00	7	0.00		
	15674.18			49		

Std. Dev. 3.70, R^2 90.50%, adjusted R^2 0.8353, predicted R^2 0.6302, C.V. % 12.03

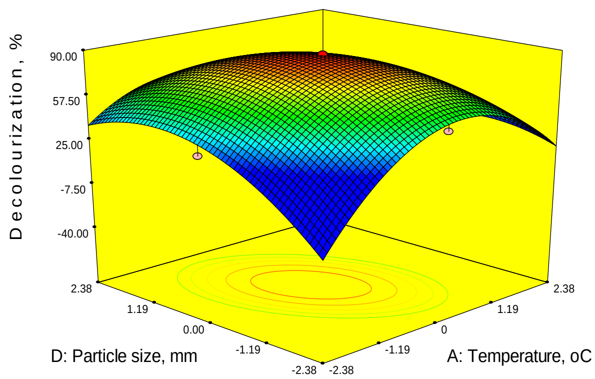

Figure 3: Response surface plot of the combined effects of temperature and agitation speed and particle size on the percentage colour removal of acid blue 9 by tamarind seed

The maximum color removal percentage of AB9 occurs at the 2.7 g / L sorbent dose and 0.17 mm particle size. The combined effect of temperature and concentration of dye was analyzed from the 3-dimensional plot of CCD representing the maximum percentage of 84 percent color removal in the 2.7 range of the sorbent dose.

Figure 9 Shows the color removal of ab9 response surface curves as a function of the contact time and agitation level. Full color removal occurs at 249 min contact time and 215 rpm. The most important environmental parameters affecting the sorption of the dye are the contact time and the speed of agitation. The maximum color removal percentage is achieved when the agitation speed is 215 rpm at a contact time of 249 min.

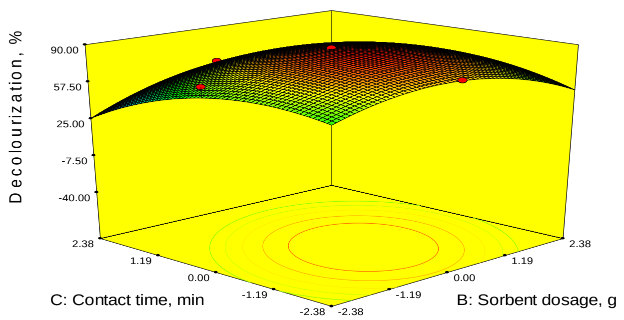

Figure 4: Response surface plot of the combined effects of temperature and particle size on the percentage colour removal of acid blue 9 by tamarind seed

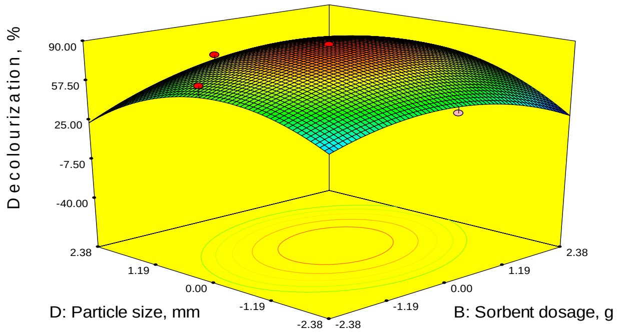

Figure 5: Response surface plot of the combined effects of sorbent dosage and contact on the percentage colour removal of acid blue 9 by tamarind seed

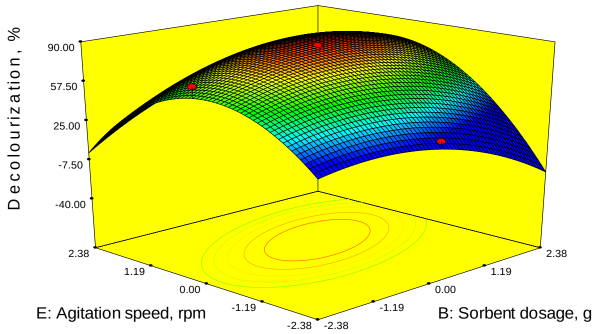

Figure 6: Response surface plot of the combined effects of sorbent dosage and particle size on the percentage colour removal of acid blue 9 by tamarind seed

Illustration 10 depicts the interaction between particle size and agitation speed, where the maximum color removal percentage was found to be 93 per cent with particle size of 0.17 mm and agitation speed of 215 rpm. In most cases, the surfaces of the reactions of the interactions between the variables were found to be elliptical.

A similar trend was observed for the removal of green malachite with tamarind seed[17]. The optimal values from these estimates are in near agreement with those obtained by optimizing the eq. (4) regression model. MATLAB 7 sequential quadratic programming is used to solve the eq. (4) polynomial regression of second degree. The sequential quadratic programming in MATLAB 7 is used to solve the second-degree polynomial regression as in eq. (4). The optimum test variable values for the encoded units are X_1 = -1.0924, X_2=-0.3004, X_3=0.7986, X_4=0.7928 and X_5=0.839 for encoded units.

They are converted into uncoded units for the actual values and the optimum values of the test variables were: Temperature – 35.5^{0}C, sorbent dosage - 2.7 g/L, contact time – 249 min, particle size -0.17 mm, stirring speed - 215 rpm. The optimal values for the variables as predicted by MATLAB were found to be within the design region. This shows that the model correctly explains the influence of the chosen variables on the percentage color removal of AB9.

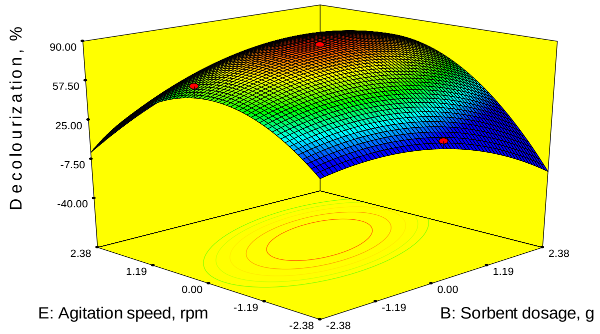

Figure 7: Response surface plot of the combined effects of sorbent dosage and agitation speed on the percentage colour removal of acid blue 9 by tamarind seed

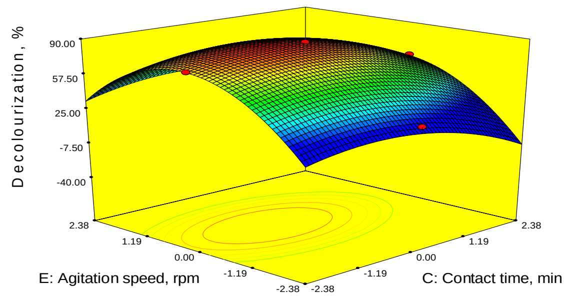

Figure 8: Response surface plot of the combined effects of contact time and particle size on the percentage colour removal of acid blue 9 by tamarind seed

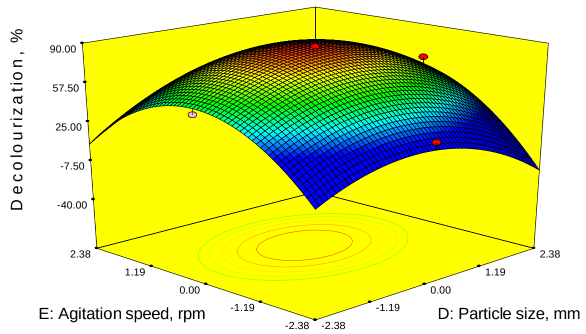

Figure 9: Response surface plot of the combined effects of contact time and agitation speed on the percentage colour removal of acid blue 9 by tamarind seed

Conclusion

In this study, tamarind seed was successfully employed for the removal of Acid blue 9 dye. The process parameters viz. temperature, adsorbent dosage, contact time, adsorbent size and agitation intensity were optimized for removal of AB9 from the aqueous medium using Response Surface (RSM) process.

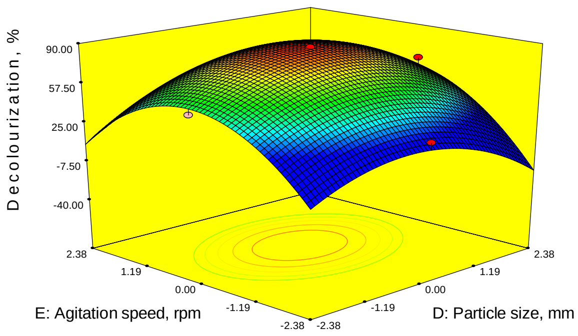

Figure 10: Response surface plot of the combined effects of agitation speed and particle size on the percentage colour removal of acid blue 9 by tamarind seed

At the optimized condition, a maximum removal found to be 89% was achieved. This is higher than the un-optimized condition. The results show a close concordance between the experimental and predicted values obtained by RSM. Hence the RSM can be effectively used to enhance the removal of dyes using adsorption.

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