STUDIES ON BIOSORPTION OF TITAN YELLOW DYE WITH DULCE POWDER AND OPTIMIZATION THROUGH CENTRAL COMPOSITE DESIGN

Dr. Ch. A. I. Raju[1] and K.Sunil[2]
[1]Assistant Professor (Stage 3), Department of Chemical Engineering, Andhra University, Visakhapatnam – 530 003, AP, INDIA
[2] Research Scholar Department of Chemical Engineering, Andhra University, Visakhapatnam – 530 003, AP, INDIA &
Asst. Professor, Department of Chemical Engineering, Semera University, Samara, Ethiopia

ABSTRACT

The major three resources like Air, Water and Food have been polluted and are seeking a special attention for their originality which has to be reestablished. The present research was investigated using dulce powder as a potential biosorbent for the removal of titan yellow. The operating parameters involved are agitation time, biosorbent size and pH of the solution, initial concentration of solution, dosage of biosorbent and temperature of the solution. The optimization was also incorporated using Central Composite Design (CCD). The optimum size of biosorbent is 53 μm, pH was obtained at 6.0 and initial concentration of Titan yellow is 20 mg/L were compared using one factor at a time with CCD. The kinetics and isotherm studies are also studied along with thermodynamic study.

Keywords *– CCD, Titan yellow, dulce powder.*

1. INTRODUCTION

With every drop of water you drink, every breath you take. Water has been used since antiquity as a symbol by which to express devotion and purity. "Water is needed for almost every aspect of energy production, from digging up fossil fuels to refining oil and generating power and the amount of water consumed by the sector is on track to double within the next 25 years, according to the International Energy Agency. Contrary to the past, our recent developed technological society has become indifferent to this miracle of life. Our natural heritage (rivers, seas and oceans) has been exploited, mistreated and contaminated. In developing nations, however, the search for safe drinking water can be a daily crisis. Within the next few decades, the lack of freshwater in certain areas of the globe will intensify and cause one of the greatest challenges to the world's population. 70.8% from earth's surface is represented by water only 2.7% is fresh water and 0.46% can be directly utilized [1]. This domestic water consumption is dwarfed by the demands of agriculture and ecosystems, even in wealthy countries where per capita domestic water consumption greatly exceeds these figures [2]. To cover all these requirements and to avoid water stress, experts generally agree that about 1,000 cubic meters of freshwater precipitate per year is needed [3]. 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. [4,5]. Various conventional processes, such as chemical precipitation, membrane filtration, ion exchange, reverse osmosis, evaporation and electrolysis, are usually applied to the treatment of industrial drainage. However, the application of such processes is often limited because of technical or economic constraints.[6] The main disadvantages are the high cost of implantation and operations for concentrations below 100 mg/L[7]. Therefore, new technologies with acceptable costs are necessary for reduction of the heavy metal concentration in industrial drainage.

2. EXPERIMENTAL PROCEDURE

The present experimentation is carried out both batch-wise and column, on biosorption of Titan yellow dye from aqueous solutions on the biosorbent – Dulce powder powder .

The experimental procedure consists of the following steps:

2.1 Preparation of the bisorbent
2.2 Characterization of biosorbent
2.3 Preparation of the stock solutions
2.3 Studies on Equilibrium Biosorption Process

2.1. Preparation of the bisorbent

Dulce fruit waste peel was collected from local fruit vendor, Visakhapatnam. The collected biosorbent was washed with water several times until the dirt particles are removed and finally washed with distilled water. The biosorbent was dried in sun light for fifteen days, cut into small pieces, powdered and sieved. In the present study, the obtained powder was used as biosorbent without any pretreatment.

2.2 Characterization of biosorbent

Biosorption of Titan yellow dye using Dulce powder powder has many affecting factors which include characterization (FTIR, XRD, SEM), Biosorbents were characterized by FTIR spectrometry using Spectrum GX of Perkin Elmer, XRD patterns were recorded from 10 to 700 For SEM studies, the dried powders and the corresponding loaded powders were first coated with ultra-thin film of gold by an ion sputter JFC-1100 and then were exposed under a Japanese make electron microscope (JEOL, JXA-8100) equilibrium studies (agitation time, biosorbent size, pH, initial concentration, biosorbent dosage, temperature), Isotherms (Langmuir, Freundlich, Temkin), Kinetics (Lagergren First Order, Pseudo Second Order), Thermodynamics (Entropy, Enthalpy and Gibb's Free Energy) and Optimization using Central Composite Design. XRD patterns were recorded from 10 to 700.

2.3 Preparation of stock solution:

The standard stock solution of titan yellow dye (1000 mg/L) was prepared by dissolving 1.0 g of 99.9 % analytical grade Titan yellow dye in 1000 mL of distilled water. The concentration of dye in the aqueous solution was varied from 20 to 200 mg/L by diluting the stock solutions with required quantity of deionized water. The pH of the working solution was adjusted using either 0.1 N HCl or 0.1N NaOH.

2.3 Studies on Equilibrium Biosorption Process:

The biosorption was carried out in a batch process by adding a pre-weighed amount of the Dulce powder powder to a known volume of aqueous solution for a predetermined time interval in an orbital shaker. The procedures adopted to evaluate the effects of various parameters via. Agitation time, biosorbent size, pH, initial concentration, biosorbent dosage and temperature of the aqueous solution on the biosorption of Titan yellow dye were evaluated using single step optimization process

Table 1.Experimental conditions for biosorption of TY dye

S.No.	Parameter	Values Investigated
1	Agitation time, t, min	5, 10, 15, 20, 25, 30, 30, 50, 60, 90, 120, 150 and 180
2	pH of the aqueous solution	2, 3, 3, 5, 6, 7 and 8
3	Initial dye concentration, Co, mg/L	20, 50, 100, 150 and 200
4	Initia Biosorbent dosage, w, g/L	10, 20, 25, 30, 35, 30, 50, 60 and 80
5	Temperature, K	283, 293, 303, 313 and 323

.

3. RESULTS AND DISCUSSIONS

In the present investigation, the prospectives of two sorbents namely Dulce powder powder and Dulce powder were evaluated to estimate their performance for the decolorization of Titan yellow dye present in aqueous solutions. The effects of parameters on decolorizationof T.Y dye were measured, data consisting of contact time, sorbent size, pH of the solution, initial concentration, sorbent dosage and temperature.

3.1. Sorption of Titan yellow dye using Dulce powder

3.2 Effect of contact time

The equilibrium contact time is determined by plotting the % dye decolorization of IC dye against contact time as shown fig. 3.1 for the interaction time intervals between 1 to 180 min. Duration of equilibrium dye decolorization is defined as the time required for dyes concentration to reach a constant value during dye decolorization. The % dye decolorization is increased briskly up to 30 min reaching 55 %. Beyond 30 min, the % sorption is constant indicating the attainment of equilibrium conditions.The maximum percentage of sorption is attained at 30 minutes. Therefore, all other experiments are conducted at this optimum contact time The maximum percentage of sorption is attained at 30 min of contact and becomes constant after 30 min indicating the attainment of the equilibrium with 53 µm size of 10 g/L sorbent dosage mixed in 50ml of aqueous solution(C_0=20 mg/L)**[8-14]**.

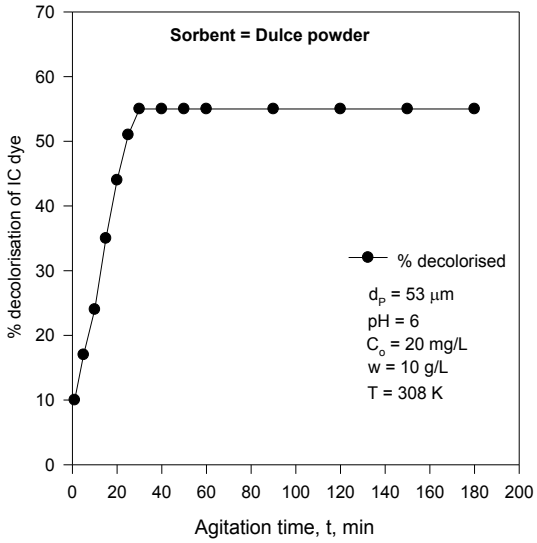


Fig3.1 Effect of contact time on % dye decolorization of IC dye

3.3 Effect of sorbent size

The variations in % dye decolorization of IC dye from the aqueous solution with sorbent size are obtained. The results are drawn in fig.3.2 with percentage dye decolorization of IC dye as a function of sorbent size.The percentage sorption is increased from 42 % to 55 % as the sorbent size decreases from 152 to 53 μm.This phenomenon is expected, as the size of the particle decreases, surface area of the sorbent enhances.The equilibrium with 30 min of time 10 g/L sorbent dosage mixed in 50ml of aqueous solution(C_0=20 mg/L)**[15-29]** .

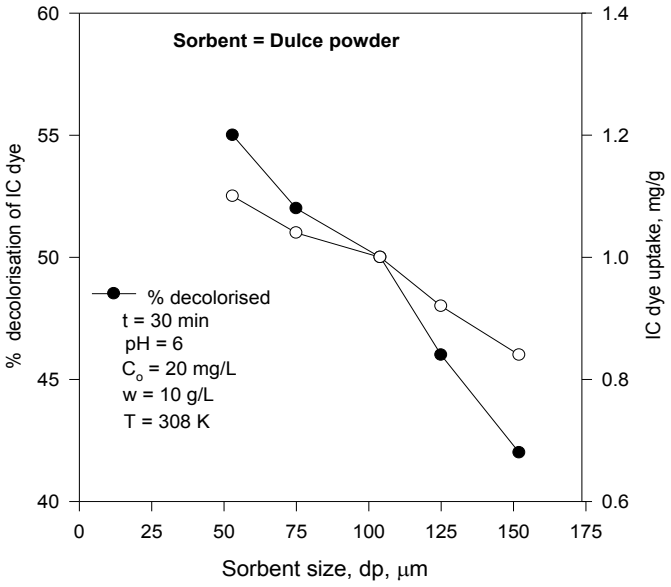


Fig. 3..2 % Dye decolorization of IC dyeas a function of sorbent size

3.3.3. Effect of pH

pH controls dye decolorization by influencing the surface change of the sorbent, the degree of ionization and the species of biosorbate. The effect of pH of aqueous solution on % dye decolorization of IC dye is shown in fig.3.3. In the present investigation, IC dye decolorization data are obtained in the pH range of 2 to 8 of the aqueous solution (C_0 = 20 mg/L) using 0.5 g of 53 μm size sorbent.The % sorption of IC dye is increased drastically from 42% to 68 % as pH is increased from 2 to 4 and beyond the pH value of 4 it decreased.

The increase in sorption capacity at higher pH may also be attributed to the reduction of H^+ ions which complete with IC dye lower pH. This is the reason for higher sorption of IC due in the pH range of 4. At pH higher than 4, precipitation of IC dye occurred and sorption is reduced **[30-39]**.

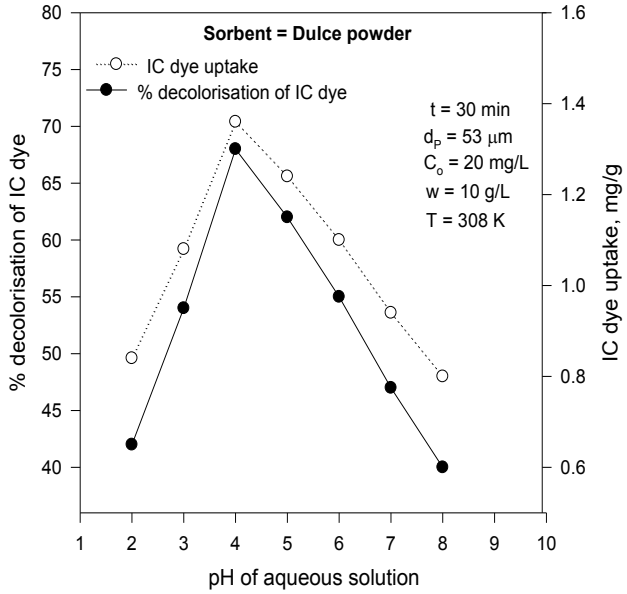


Fig. 3.3 Observation of pH along with % dye decolorization of IC dye

3.4. Effect of initial concentration

The experiments were carried out using various concentrations of IC dye in the aqueous solution under the optimum size, pH values and equilibrium contact time. The effect of initial concentration of IC dye in the aqueous solution on the percentage dye decolorization of IC dye is shown in fig.3.4.The percentage sorption of IC dye is decreased from 68 %to 40 % with an increase in C_0 from 20 mg/L to 200 mg/L.The equilibrium with 30 min of time 10 g/L sorbent dosage with 53 μm size mixed in 50ml of aqueous solution **[40-49]**.

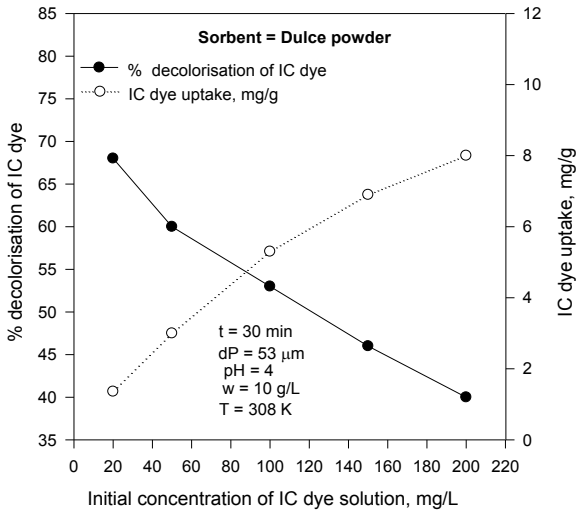


Fig. 3.4 Variationof initial concentration with % dye decolorization of IC dye

3.5 Effect of sorbent dosage

The percentage dye decolorization of IC dye is drawn against sorbent dosage for 53 μm size sorbent in fig.3.5. The percentage sorption increased with increase in sorbent dosage.

The sorption of IC dye increased from 68 % to 88 % with an increase in sorbent dosage from 0.5 to 1.25g (25g/L).The change in percentage decolorization of IC dye is marginal from 88 % to 93 % when 'w' is increased from 1.25 to 4 g. Hence all other experiments are conducted at 1.25 g dosage**.** The equilibrium with 30 min of time 4 pH with 53 μm size mixed in 50ml of aqueous solution **[50-59]**.

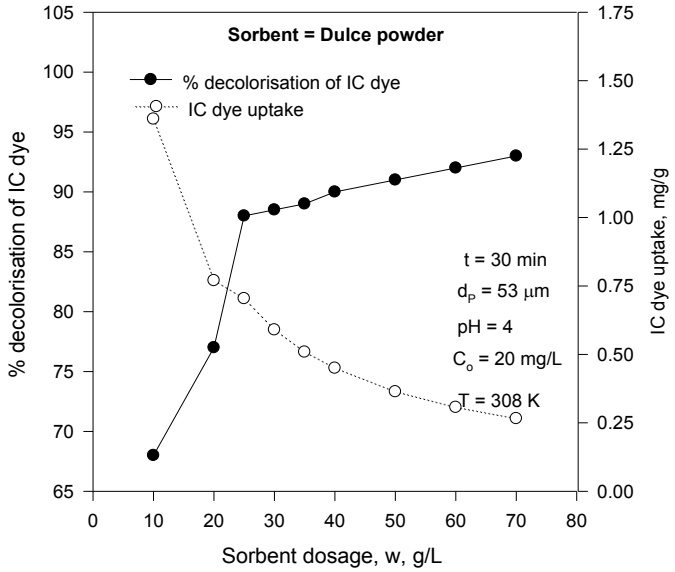


Fig. 3.5 Dependency of % dye decolorization of IC dye on sorbent dosage

3.6 Effect of Temperature

The effect of temperature on the equilibrium dye uptake was significant. The effect of changes in the temperature (283, 293,303, 313, and 323) on the IC dye uptake is shown in Fig.4.40. When temperature was lower than 303 K, IC dye uptake increased with increasing temperature, but when temperature was over 303 K, the results were more or less constant.

The increase in the percentage sorption with the rise in temperature may be due to the increase in chemical interaction between IC dye ions and further increase to 323 K is marginal from 303K. High temperature favors the diffusion of dye molecules in the internal porous structure of surface. The equilibrium with 30 min of time 25g/L sorbent dosage with 53 μm size mixed in 50ml of aqueous

Solution. The sorption capacity of dye is increased at higher temperatures, which indicates that sorption of dyes in this system is an endothermic process **[60-69]**.

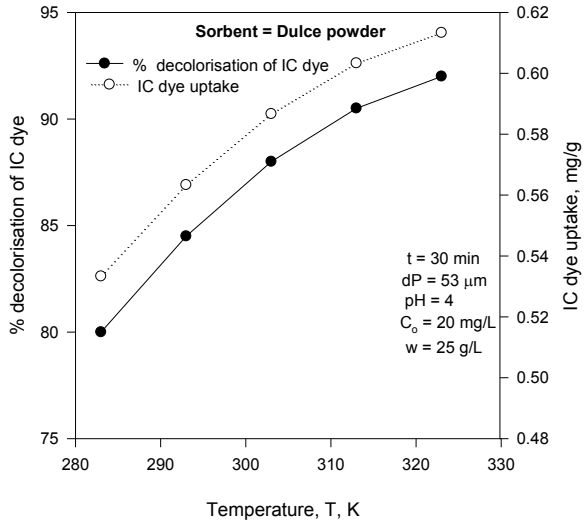


Fig.3.6 Effect of temperature on % dye decolorization of IC dye

3.7 Equilibrium isotherm models

Langmuir, Freundlich and Temkin models are used to find the equilibrium relationships between the sorbents and the sorbate. For all these models, non-linear regression methods are followed to obtain the isothermal constants.

The Langmuir relationship is hyperbolic and the equation is

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

Equation can be rearranged as

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

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 $R_L = 1/ (1+bC_e)$
The equation obtained 'n' $C_e/q_e = 0.0880\ C_e + 4.56451$ with a good linearity (correlation coefficient, R^2~0.99488) indicating strong binding of IC dye to the surface of dulce powder.

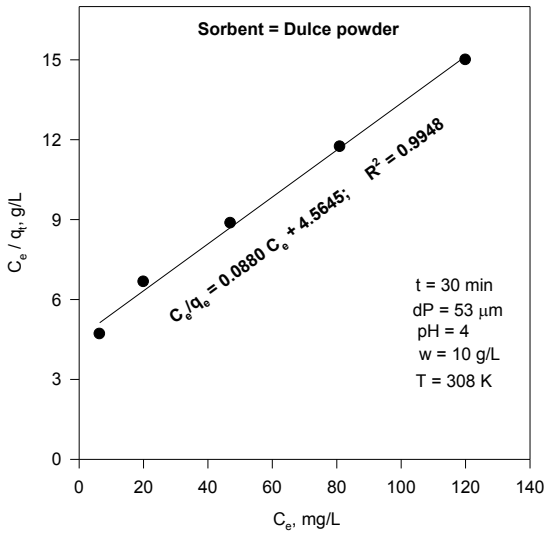


Fig. 3.7 Langmuir isotherm for % dye decolorization of IC dye

Freundlich isotherm:
Freundlich presented an empirical dye decolorization 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
$q_e = K_f C_e^{\ n}$
Where K_f (mg) represents the sorption capacity when dye equilibrium concentration and n represents the degree of dependence of sorption with equilibrium concentration
Taking logarithms on both sides, we get
$\ln q_e = \ln K_f + n \ln C_e$
Freundlich isotherm is drawn between $\ln C_e$ and $\ln q_e$. The resulting equation has a correlation coefficient of 0.99148.
$\ln q_e = 0.6147 \ln C_e - 0.7818;$
The 'n' value in the above equations satisfies the condition of $0<n<1$ indicating favorable sorption.

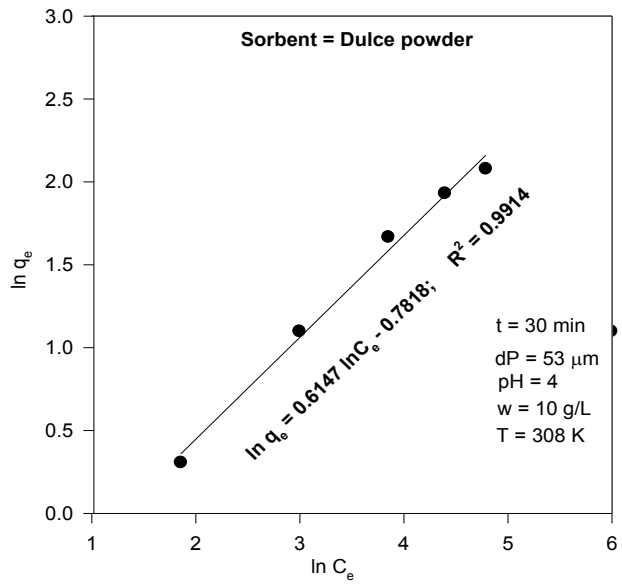


Fig. 3.8 Freundlich isotherm for % dye decolorization IC dye

Temkin isotherm:
Temkin and Pyzhev isotherm equation describes the behavior of many sorption 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
$q_e = (RT/ b_T) \ln(A_T) + (RT/b_T) \ln(C_e)$
The equation obtained for IC dye sorption is
$q_e = 2.7971 \ln C_e - 5.4081$ with a correlation coefficient 0.9996.
The best fit model is determined based on the linear regression correlation coefficient (R).

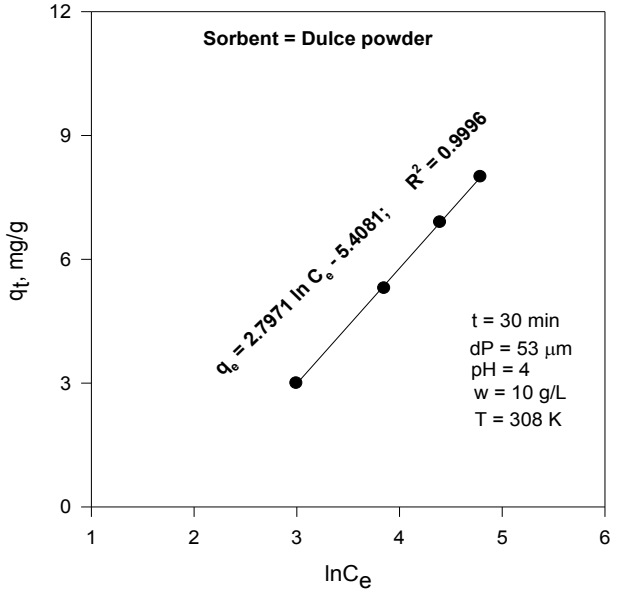


Fig. 3.9 Temkin isotherm for % dye decolorization of IC dye

It is found that sorption data are well represented by Temkin isotherm with higher correlation coefficient of 0.9996, followed by Langmuir and Freundlich isotherms with correlation coefficients of 0.99488 and 0.99148 respectively**[70-84]**.

Table – 3.1 Isotherm constants (linear method)

Langmuir isotherm	Freundlich isotherm	Temkin isotherm
q_m = 11.35912 mg/g	K_f = 0.457582 mg/g	A_T = 0.144646 L/mg
R_L = 0.890127	n = 0.61472	b_T = 915.4882
R^2 = 0.99488	R^2 = 0.99148	R^2 = 0.9996

3.8 Kinetics of dye decolorization

Psudo first order, second order and intra-particle diffusion kinetic models have been used to describe the rate of metal ions uptake. Pseudo first and second order plots are shown in Figs. 3.10 to 3.11. The rate constants and correlation coefficients are indicated in Table 4.19.

Based on regression coefficients (great that0.99) and the similarity between calculated and experimental q_e values,

the best kinetic model for adsorption of lead and copper was identified as pseudo-second order model. The best fit of the experimental data to the pseudo second order suggest that the adsorption process is a chemical sorption involving valence forces through sharing or exchange of electrons between the sorbent and the sorbate.

The order of biosorbate – biosorbent interactions have been described using kinetic model.

Traditionally, the first order model of Lagergren finds wide application. In the case of sorption preceded by diffusion through a boundary, the kinetics in most cases follows the first order rate equation of Lagrangen:

$(dq_t/dt) = K_{ad} (q_e - q_t)$ where q_e and q_t are the amounts adsorbed at t, min and equilibrium time and K_{ad} is the rate constant of the pseudo first order sorption.

The above equation can be presented as

$\int (dq_t/(q_e - q_t)) = \int K_{ad}\, dt$

Applying the initial condition $q_t = 0$ at $t = 0$, we get

$\log (q_e - q_t) = \log q_e - (K_{ad}/2.303)\, t$

$\log (q_e - q_t) = 0.0711 - 0.0183\, t$

Plot of $\log (q_e - q_t)$ versus 't' gives a straight line for first order kinetics, facilitating the computation of adsorption rate constant (K_{ad}).

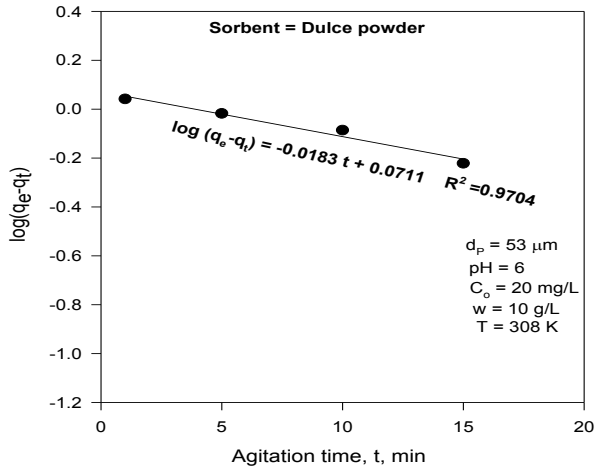


Fig. 3.10 first order kinetics for % dye decolorization of IC dye

pseudo second order kinetic equation:

$(dq_t/dt) = K (q_e - q_t)^2$ is applicable,

where 'K' is the second order rate constant.

The other form of the above equation is:

$(dq_t/(q_e - q_t)^2) = Kdt$

$1/x = K x + C$

$C = 1/q_e$ at $t = 0$ and $x = q_e$

Substituting these values in above equation, we obtain:

$1/(q_e - q_t) = Kt + (1/q_e)$

Rearranging the terms, we get the linear form as:

$(t/q_t) = (1/Kq_e^2) + (1/q_e)\, t.$

$(t/q_t) = 0.0183\, t + 0.0711.$

The pseudo second order model based on above equation, considers the rate -limiting step as the formation of chemisorptive bond involving sharing or exchange of electrons between the sorbate and sorbent. If the pseudo second order kinetics is applicable, the plot of (t/q_t) versus 't' gives a linear relationship that allows computation of q_e and K.

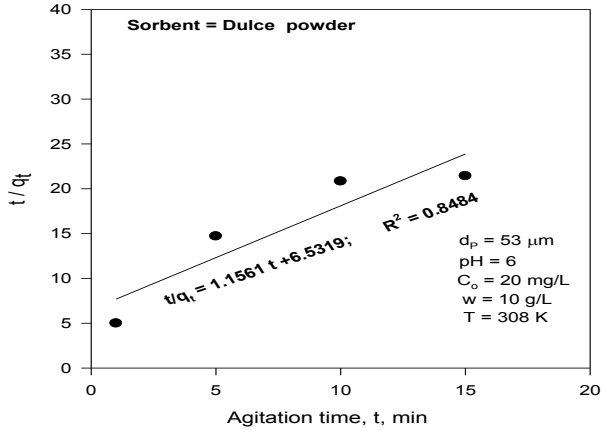


Fig. 3.11 second order kinetics for % dye decolorization of IC dye

In the present study, the kinetics are investigated with 50 mL of aqueous solution (C_0= 20 mg/L) at 303 K with the interaction time intervals of 1 min to 180 min. Lagragen plots of log (q_e-q_t) versus contact time (t) for decolorization of IC dye the sorbent size (53 μm) of *dulce* powder in the interaction time intervals of 1 to 180 min **[85-94]**.

Table–3.2 Equations and rate constants

Order	Equation	Rate constant	R^2
Lagergren first order	log (q_e-q_t) = – 0.01837 t +0.0711	0.042145 min^{-1}	0.9704
Pseudo Second order	t/q_t = 1.1561 t + 6.5319	0.2046 g/(mg-min)	0.8484

3.9. Thermodynamics of dye decolorization

sorption is temperature dependant. In general, the temperature dependence is associated with three thermodynamic parameters namely change in enthalpy of sorption ((ΔH), change in entropy of sorption (ΔS) and change in Gibbs free energy (ΔG).

The Vant Hoff's equation is

log (q_e /C_e) = ΔH/(2.303 RT) + (ΔS/2.303 R)

log (q_e /C_e) = – 1.0627 (1 / T) + 2.8866

Where (q_e/C_e) is called the sorption affinity.

If the value of ΔS is less than zero, it indicates that the process is highly reversible. If ΔS is more than or equal to zero, it indicates the reversibility of process.

The negative value for ΔG indicates the spontaneity of sorption. Whereas the positive value indicates is non spontaneity of sorption.

Experiments are conducted to understand the sorption behavior varying the temperature from 283 to 323 K. The Vant Hoff's plot (fig. 3.12) for the sorption data obtained for IC dye using Dulce powder **[95-109]**.

The values are

ΔG = -17002.9,

ΔH = 20.34767and

ΔS = 55.27014

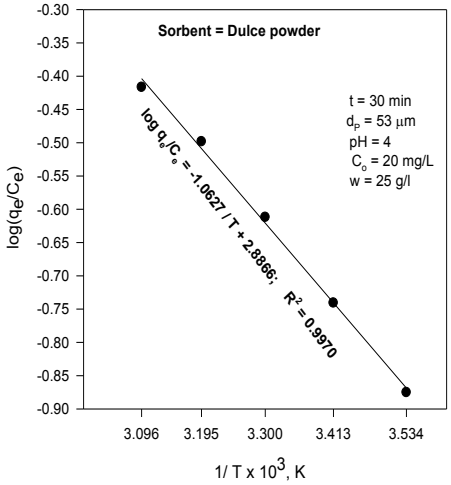


Fig 3.12 Vantoff's plot for % dye decolorization of IC dye

3.10 Optimization of the parameters using CCD

In order to determine an optimum condition for IC dyedecolorization, the parameters having greater influence over the response is to be identified. In the present study, the relationship between four independent variables and percent of IC dye decolorized fitted well with the quadratic model.The regression equation for the optimization of medium constituents: % decolorization of IC dye (*Y*) is function of the pH (X_1), C_o (X_2), w (X_3), and T (X_4).

The effects of four independent variables (sorbent dosage, initial concentration of IC dye in aqueous solution, pH and temperature) on IC dye sorption are analyzed using Central Composite Design (CCD) **[110-119]**.

The optimum conditions for the four independent variables on the extent of IC dye sorption are formed within the quadratic model.

Regression equation for the optimization of sorption is

% sorption of IC dye(*Y*) is function of pH of aqueous solution (X_1), initial IC dye concentration (X_2), dosage (X_3), and Temperature of aqueous solution (X_4).

The multiple regression analysis of the experimental data has yield the following equation:

$$\mathbf{Y = –1562.29 – 25.28\ X_1 + 2.18\ X_2 + 5.67\ X_3 + 9.96\ X_4 – 3.52\ X_1^2 – 0.08X_2^2 –0.08X_3^2 – 0.02\ X_4^2 - 0.05\ X_1X_2 + 0.000\ X_1X_3 – 0.01\ X_1X_4 + 0.01\ X_2X_3 + 0.000\ X_2X_4 – 0.01\ X_3X_4}$$

Table–3.4 Results from CCD for IC dyedecolorization by Dulce powder

Run No.	% sorption of IC Dye	
	Experimental	Predicted
1	84.68	84.67
2	85.52	85.56
3	86.18	86.15
4	85.79	85.80
5	82.82	82.81
6	84.22	84.17
7	85.38	85.40
8	85.54	85.51
9	83.39	83.40
10	84.72	84.69
11	84.89	84.93
12	84.98	84.97
13	80.66	80.63
14	82.38	82.39
15	83.32	83.27
16	83.78	83.78
17	80.69	80.71
18	77.69	77.71
19	87.02	87.00
20	83.89	83.95
21	84.09	84.11
22	86.98	86.99
23	86.08	86.10
24	87.48	87.50
25	93.3	93.30
26	93.3	93.30
27	93.3	93.30
28	93.3	93.30
29	93.3	93.30
30	93.3	93.30

Regression equation for the optimization of sorption is % sorption of IC dye(Y) is function of pH of aqueous solution (X_1), initial IC dye concentration (X_2), dosage (X_3), and Temperature of aqueous solution (X_4).
The multiple regression analysis of the experimental data has yield the following equation:

$$\mathbf{Y = -1562.29 - 25.28\ X_1 + 2.18\ X_2 + 5.67\ X_3 + 9.96\ X_4 - 3.52\ X_1^2 - 0.08X_2^2 - 0.08X_3^2 - 0.02\ X_4^2 - 0.05\ X_1X_2 + 0.000\ X_1X_3 - 0.01\ X_1X_4 + 0.01\ X_2X_3 + 0.000\ X_2X_4 - 0.01\ X_3X_4}$$

Each contour plot represents a number of combinations of two test variables with the other variable maintained at zero levels. The maximum percentage dye decolorization of cadmium is indicated by the surface confined in the smallest curve (circular or elliptical) of the contour plot.

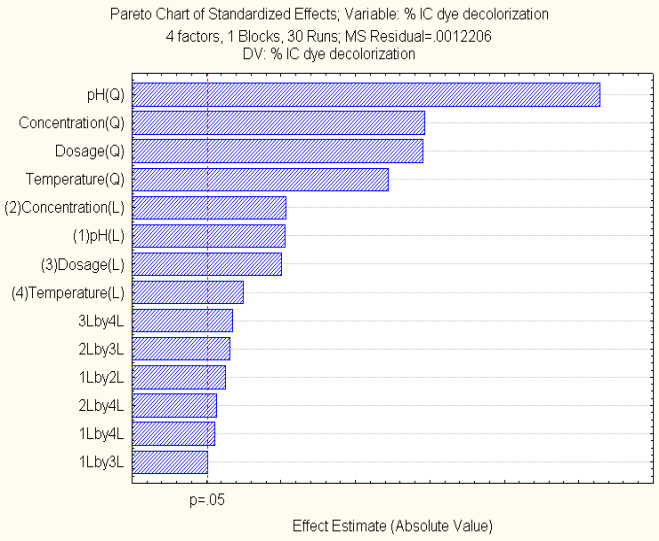


Fig. 3.13 pareto Chart

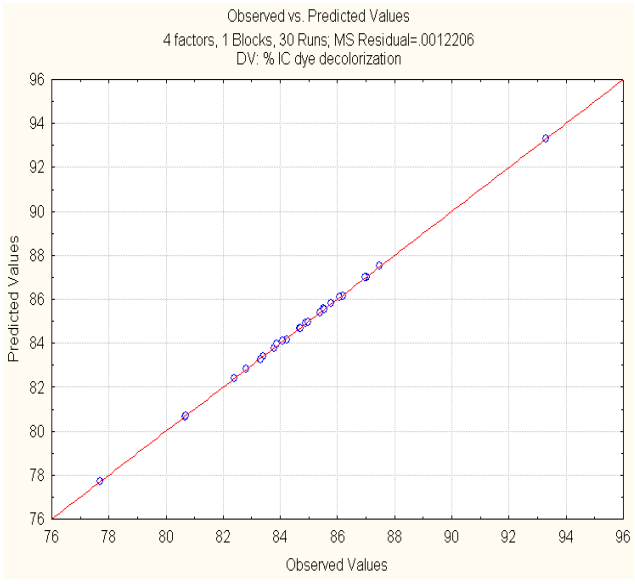
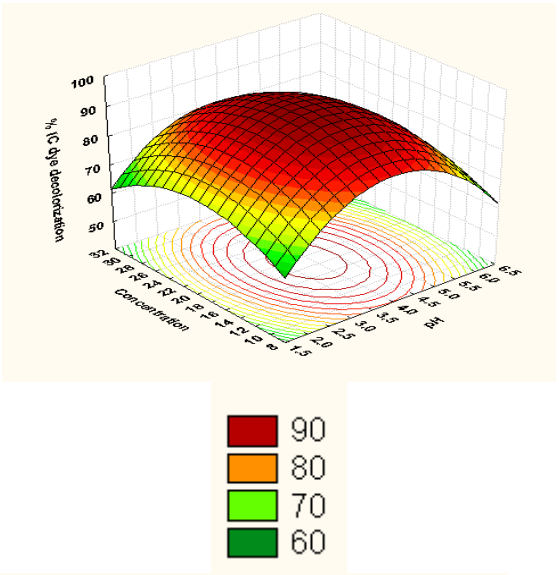
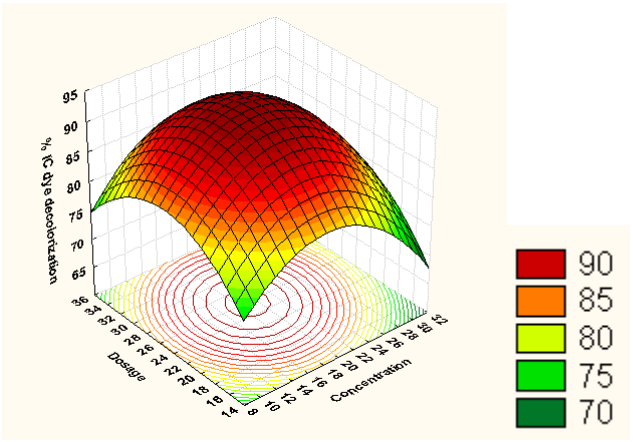
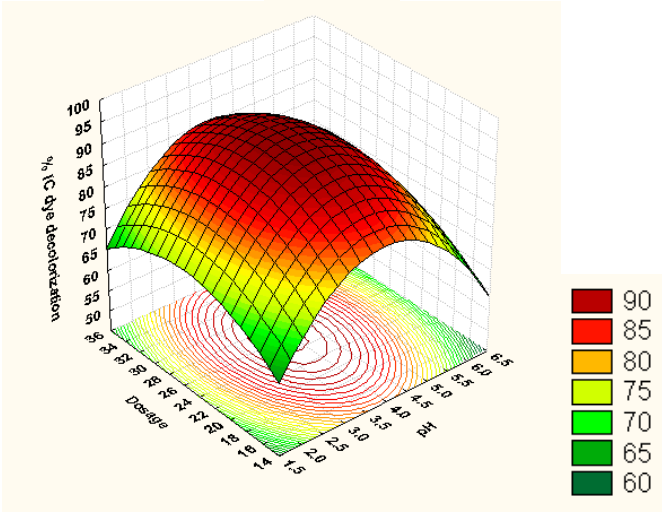
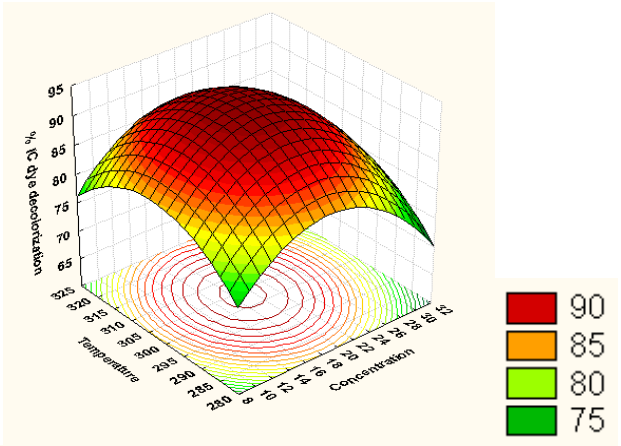


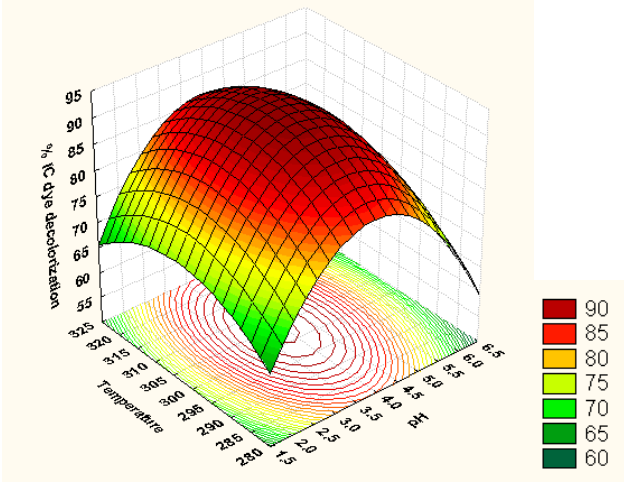
Fig.3.14 Normal Probability Plot

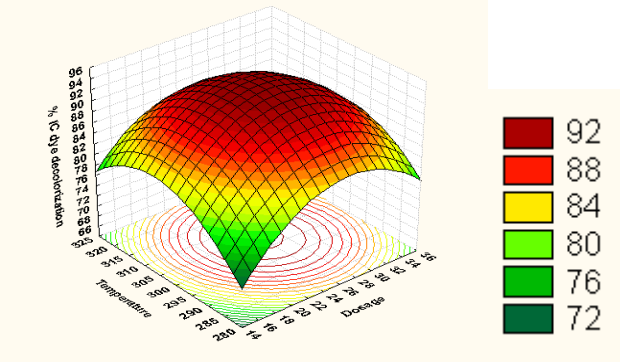












Figs. 3.15 (a)-3.15 (f) represents the contour plots for the optimization of % dye decolorization of IC dye using Dulce powder

Table-3.7 Comparison between optimum values from CCD and experimentation

Variable	CCD	Experimental
pH of aqueous solution	3.9006	4
Initial IC dye concentration, mg/L	19.1251	20
Sorbent dosage, w, g/L	25.8310	25
Temperature, K	303.8257	303
% biosorption	93.478	88

3.11 Characterization of *dulce* powder

3.11.1 FTIR spectrum of untreated *dulce* powder

FTIR spectrum for un treated powder is shown in fig 4.50(a). A broad band at 623.12 cm^{-1} is due to the presence of 2,4 benzene deformation out of phase. The broad absorption peaks at around 771.40 cm^{-1} indicates the presence of Weak benzene ring deformation.The band at 1060.33cm^{-1}due to C–H bending vibrations. The band at 1322.94cm^{-1} denotes presence of –CH2 bending vibrations. The band at 1379.86cm^{-1}due to the presence of $–CH_2$ bending vibrations. The band at 1443.46cm^{-1}suggests the presence of C–N stretching. The band at 1532.14cm^{-1} due to the presence of Amide N–H bending vibrations. The band at 1642.80cm^{-1} indicates the presence of Oleifinic C = C and Carbonyl C = O stretching. The band at 2926.84cm^{-1} due to the presence of -CH2 stretching vibrations.the band at 3397.53cm^{-1} due O-H-stretching modes. The shifts in FTIR peaks are shown in table-4.25.

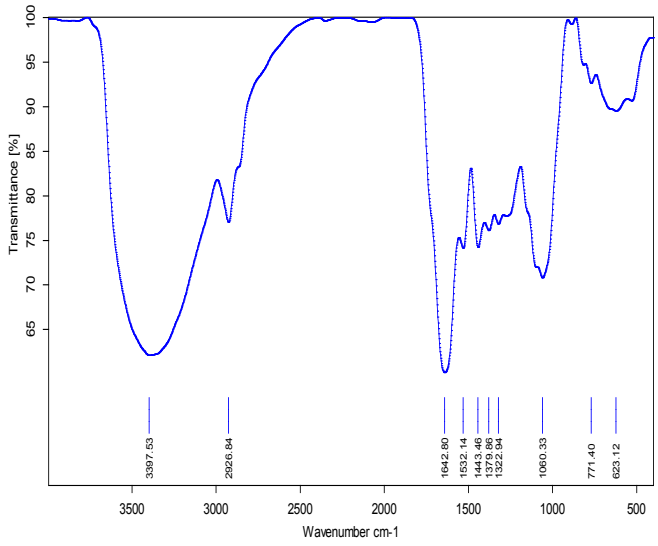


Fig. 3.16 (a) FTIR spectrum of untreated *Dulce* powder

3.11.2 FTIR spectrum of IC dye treated *Dulce* powder

FTIR spectrum for treated powder is shown in fig 4.50(b). Broad band at 622.02 cm^{-1} suggests 2,4 benzene deformation out of phase. The band at 774.07 cm^{-1} is due to the presence of Weak benzene ring deformation. The band at 1059.88 cm^{-1} indicates the presence of C–H bending vibrations. The band at 1277.03 cm^{-1} denotes the -SO3 stretching. Broad band at 1377.62 cm^{-1} suggests –CH2 bending vibrations. The band at 1443.46cm^{-1}due to the presence C–N stretching. The band at 1531.55cm^{-1}suggests the presence of Amide N–H bending vibrations. The band at 1642.63cm^{-1} due to the presence of Oleifinic C = C and Carbonyl C = O stretching. The band at 2372.43cm^{-1} indicates the presence of C ≡ N in the polyacrylnitrile. The band at 2926.26cm^{-1} due to the presence of CH2 stretching vibrations. the band at 3381.77cm^{-1} due to O-H-stretching modes**[120-129]**. The shifts in FTIR peaks are shown in table-4.25.

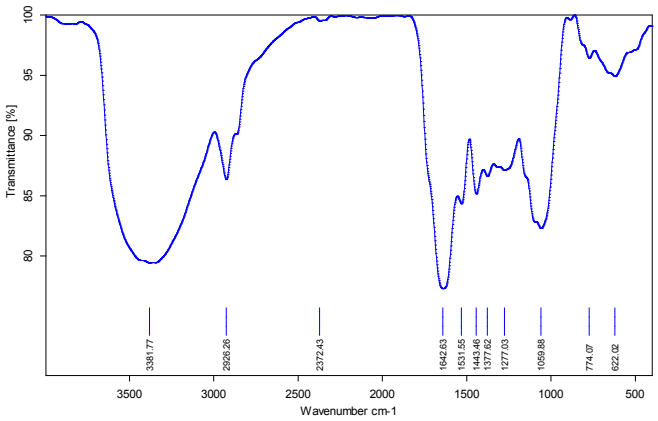


Fig. 3.16 (b) FTIR spectrum of IC treated *Dulce* powder

Table-3.8 Shift of FTIR peaks for untreated and IC dye treated Dulce powder

Sl No	Before sorption Untreated Dulce	After sorption IC treated Dulce	Band
1	623.12		2,4 benzene deformation out of phase
2		622.02	2,4 benzene deformation out of phase
3	771.40		Weak benzene ring deformation
4		774.07	Weak benzene ring deformation

5	1060.33		C–H bending vibrations
6		1059.88	C–H bending vibrations
7	1322.94		–CH2 bending vibrations
8		1277.03	-SO3 stretching
9	1379.86		–CH2 bending vibrations
10		1377.62	–CH2 bending vibrations
11	1443.46		C–N stretching
12		1443.46	C–N stretching
13	1532.14		Amide N–H bending vibrations
14		1531.55	Amide N–H bending vibrations
15	1642.80		Oleifinic C = C and Carbonyl C = O stretching
16		1642.63	Oleifinic C = C and Carbonyl C = O stretching
17	2926.84		CH2 stretching vibrations
18		2372.43	C ≡ N in the polyacrylnitrile
19	3397.53		O-H-stretching modes
20		2926.26	CH2 stretching vibrations
21			
22		3381.77	O-H-stretching modes

3.11.3 XRD spectrum of untreated dulcepowder

X-ray diffractogram of the untreated dulce powder is observed and the XRD pattern does not exhibit apparently crystalline nature. The peaks at 2θ values of 19.13, 18.70, 15.58, 15.91 and 18.53 corroborate the presence of $C_{36}I_6N_{12}S_3Zn_3$, $F_{39}S_{69}Se_4$, $C_{16}AlCuF_{36}O_4P_8$, CS_2O_7 and $Co_2H_{33}N_{10}O_{18}S_4$. Their corresponding d-values are 0.9413, 0.9248, 0.9212, 0.9008 and 0.8936.

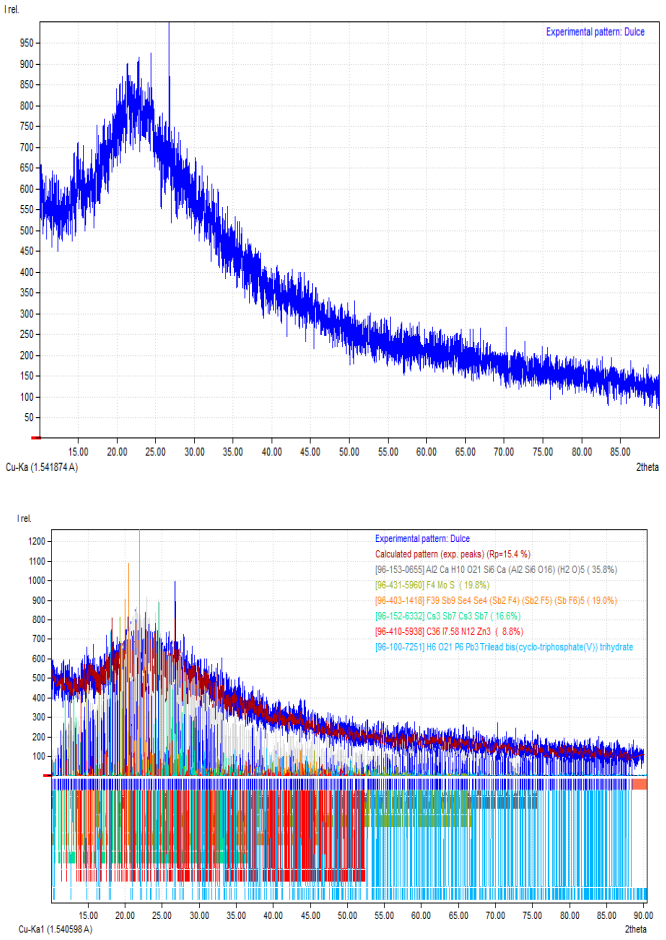
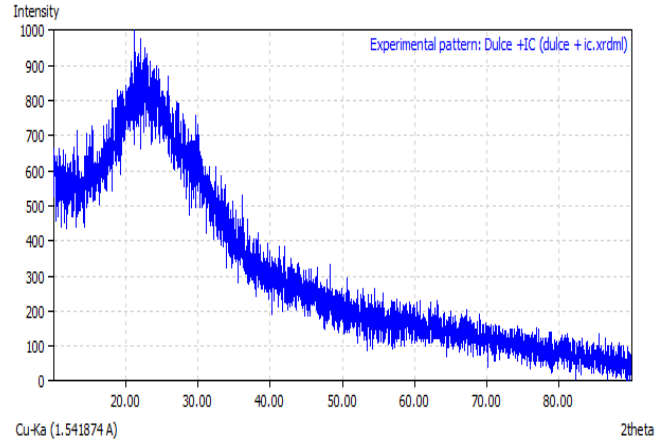


Fig. 3.17 (a) XRD spectrum of untreated dulce powder.

3.11.4 XRD spectrum of treated dulce powder

XRD patterns of IC dye treated with dulce show very spiky and clear peaks and exhibit absolutely amorphous nature. The peaks at 2θ values of 13.43, 14.60, 16.32, 19.59 and 12.23 corroborate the presence of $C_{36}I_6N_{12}S_3Zn_3$, $Cs_6InP_3S_{13.5}$, $As_2F_{12}S_8$, $CF_{20}O_4Te_4$ and $F_{20}Kr_5Sb_2$ (graphite). Their corresponding d-values are 0.9342, 0.9345, 0.9254, 0.9141 and 0.9123 respectively **[130-134]**.



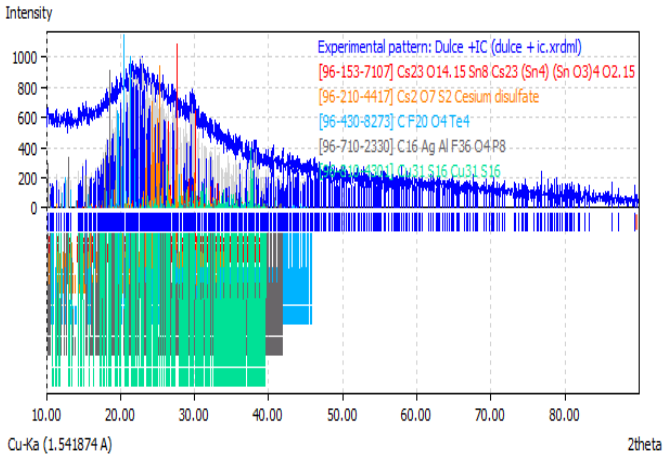


Fig. 3.17 (b) XRD spectrum of treated dulce powder

4. CONCLUSIONS:

1. The equilibrium agitation time for TY dye sorption is 50 min.
2. With an increase in the initial concentration of TY dye (20 to 200 mg/L) in the aqueous solution, the percentage sorption of TY dye from the aqueous solution is decreased (60 to 40 %).
3. Optimum pH value is 6 (1.2 mg/g).
4. The CCD optimized conditions are: w = 31.9071 g/L, pH = 6.0179, Co = 18.3596 mg/L and T = 306.2826 with % dye decolorization of 90.36656%.
5. The sorption of TY dye is better described by lagergren first order kinetics (K1 = – 0.055272 g/mg-min, R2 = 0.9731).
6. The experimental data are well represented by Freundlich isotherm (R2 = 0.9868).
7. The thermodynamic investigation reveals:the endothermic nature of sorption (ΔH = 9.533362 J/mole). irreversibility of sorption (ΔS = 17.00458 J/mole-K) and increased randomness at the solid/solution interface.
8. The spontaneity and feasibility of sorption (ΔG = -5227.88J/mole).

ACKNOWLEDGEMENTS

The Author expresses his deep sense of gratitude to Andhra University and Department of Chemical Engineering for providing chemicals, equipment and laboratory facilities.

REFERENCES

[1]. Sahadevan Renganathan, Venkatakrishnan R, Gautam and Velan Manickam P, "Kinetic Studies on Sorption of Textile Dyes Using Lamina and Petiole Parts of Eichhornia crassipes", Chemical Product and Process Modeling, 3:2, 2008.

[2]. Isbela Michael aex,"learning about importance of water for life through informatics products"2012.

[3]. Howard G, Bartram J (2003) Domestic WaterQuantity, Service Level and Health. Geneva:

[4]. World Health Organisation, Available: http://whqlibdoc.who.int/hq/2003/WHO_SDE_WSH_03.02.pdf. Accessed May 2009.3. Data 360 (2010) Average water uses per person perday.

[5]. Periasamy K, Namasivayam C. Process development forremoval and recovery of cadmium from wastewater by alow-cost adsorbent: adsorption rates and equilibrium studies.

[6]. Suzuki Y, Kametani T, Maruyama T. Removal of heavymetals from aqueous solution by nonliving Ulva seaweed as biosorbent. Water Res. 2005; 39:1803–1808.

[7]. Yilmaz M, Tay T, Kivanc M, Turk H. Removal of copper (II) ions from aqueous solution by a lactic acid bacterium.

[8]. Braz J Chem Eng. 2010;27(2):309–314. http://dx.doi.org/10.1590/S0104-66322010000200009

[9]. Borba CE, Guirardello R, Silva EA, Veit MT, TavaresCRG. Removal of nickel (II) ions from aqueous solution bybiosorption in a fixed bed column: experimental and theoreticalbreakthrough curves. Biochem Eng J. 2006;30:184–191

[10]. Sahadevan Renganathan, Venkatakrishnan R, Gautam and Velan Manickam P, "Kinetic Studies

on Sorption of Textile Dyes Using Lamina and Petiole Parts of Eichhornia crassipes", Chemical Product and Process Modeling, 3:2, 2008.

[11]. Ho, Yuh-Shan, and Gordon McKay. "Pseudo-second order model for sorption processes." Process biochemistry 34, no. 5 (1999): 451-465.

[12]. Pavan, Flavio Andre, Ana Cristina Mazzocato, and Yoshitaka Gushikem. "Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent." Bioresource technology 99, no. 8 (2008): 3162-3165.

[13]. Mall, Indra D., Vimal C. Srivastava, and Nitin K. Agarwal. "Removal of Orange-G and Methyl Violet dyes by adsorption onto bagasse fly ash—kinetic study and equilibrium isotherm analyses." Dyes and pigments 69, no. 3 (2006): 210-223.

[14]. Karcher, Silke, Anja Kornmüller, and Martin Jekel. "Anion exchange resins for removal of reactive dyes from textile wastewaters." Water Research 36, no. 19 (2002): 4717-4724.

[15]. Gong, Renmin, Youbin Jin, Fayang Chen, Jian Chen, and Zhili Liu. "Enhanced malachite green removal from aqueous solution by citric acid modified rice straw." Journal of hazardous materials 137, no. 2 (2006): 865-870.

[16]. Robinson, T., B. Chandran, and P. Nigam. "Effect of pretreatments of three waste residues, wheat straw, corncobs and barley husks on dye adsorption." Bioresource technology 85, no. 2 (2002): 119-124.

[17]. Saeed, Asma, Mehwish Sharif, and Muhammad Iqbal. "Application potential of grapefruit peel as dye sorbent: kinetics, equilibrium and mechanism of crystal violet adsorption." Journal of Hazardous Materials 179, no. 1 (2010): 564-572.

[18]. Gupta, Vinod Kumar, Rajeev Jain, and Shaily Varshney. "Removal of Reactofix golden yellow 3 RFN from aqueous solution using wheat husk—an agricultural waste." Journal of Hazardous Materials 142, no. 1 (2007): 443-448.

[19]. Ho, Y. S., and G. McKay. "The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat." The Canadian Journal of Chemical Engineering 76, no. 4 (1998): 822-827.

[20]. Khaled, Azza, Ahmed El Nemr, Amany El-Sikaily, and Ola Abdelwahab. "Removal of Direct N Blue-106 from artificial textile dye effluent using activated carbon from orange peel: adsorption isotherm and kinetic studies." Journal of Hazardous Materials 165, no. 1 (2009): 100-110.

[21]. Ho, Yuh-Shan, Chun-Chiao Chiang, and Yung-Chien Hsu. "Sorption kinetics for dye removal from aqueous solution using activated clay." Separation Science and Technology 36, no. 11 (2001): 2473-2488.

[22]. Guibal, Eric. "Interactions of metal ions with chitosan-based sorbents: a review." Separation and Purification Technology 38, no. 1 (2004): 43-74.

[23]. Saeed, Asma, Mehwish Sharif, and Muhammad Iqbal. "Application potential of grapefruit peel as dye sorbent: kinetics, equilibrium and mechanism of crystal violet adsorption." Journal of Hazardous Materials 179, no. 1 (2010): 564-572.

[24]. McKay, G., J. F. Porter, and G. R. Prasad. "The removal of dye colours from aqueous solutions by adsorption on low-cost materials." Water, Air, & Soil Pollution 114, no. 3 (1999): 423-438.

[25]. Hameed, B. H., and H. Hakimi. "Utilization of durian (Durio zibethinus Murray) peel as low cost sorbent for the removal of acid dye from aqueous solutions." Biochemical Engineering Journal 39, no. 2 (2008): 338-343.

[26]. Ferrero, Franco. "Dye removal by low cost adsorbents: Hazelnut shells in comparison with wood sawdust." Journal of Hazardous Materials 142, no. 1 (2007): 144-152.

[27]. Robinson, T., B. Chandran, and P. Nigam. "Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk." Environment International 28, no. 1 (2002): 29-33.

[28]. Ong, S. T., C. K. Lee, and Z. Zainal. "Removal of basic and reactive dyes using ethylenediamine modified rice hull." Bioresource technology 98, no. 15 (2007): 2792-2799.

[29]. Janoš, Pavel, and Veronika Šmídová. "Effects of surfactants on the adsorptive removal of basic dyes from water using an organomineral sorbent—iron humate." Journal of colloid and interface science 291, no. 1 (2005): 19-27.

[30]. Chuah, T. G., A. Jumasiah, I. Azni, S. Katayon, and SY Thomas Choong. "Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview." Desalination 175, no. 3 (2005): 305-316.

[31]. Gong, Renmin, Youbin Jin, Fayang Chen, Jian Chen, and Zhili Liu. "Enhanced malachite green

removal from aqueous solution by citric acid modified rice straw." Journal of hazardous materials 137, no. 2 (2006): 865-870.

[32]. Ho, Yuh-Shan, Chun-Chiao Chiang, and Yung-Chien Hsu. "Sorption kinetics for dye removal from aqueous solution using activated clay." Separation Science and Technology 36, no. 11 (2001): 2473-2488.

[33]. Chuah, T. G., A. Jumasiah, I. Azni, S. Katayon, and SY Thomas Choong. "Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview." Desalination 175, no. 3 (2005): 305-316.

[34]. Ofomaja, Augustine E., and Yuh-Shan Ho. "Equilibrium sorption of anionic dye from aqueous solution by palm kernel fibre as sorbent." Dyes and Pigments 74, no. 1 (2007): 60-66.

[35]. Tunc, Özlem, Hacer Tanacı, and Zümriye Aksu. "Potential use of cotton plant wastes for the removal of Remazol Black B reactive dye." Journal of Hazardous Materials 163, no. 1 (2009): 187-198.

[36]. Janoš, Pavel, Sezen Coskun, Věra Pilařová, and Jaroslav Rejnek. "Removal of basic (Methylene Blue) and acid (Egacid Orange) dyes from waters by sorption on chemically treated wood shavings." Bioresource Technology 100, no. 3 (2009): 1450-1453.

[37]. Gong, Renmin, Youbin Jin, Jian Chen, Yun Hu, and Jin Sun. "Removal of basic dyes from aqueous solution by sorption on phosphoric acid modified rice straw." Dyes and Pigments 73, no. 3 (2007): 332-337.

[38]. Forgacs, Esther, Tibor Cserhati, and Gyula Oros. "Removal of synthetic dyes from wastewaters: a review." Environment international 30, no. 7 (2004): 953-971.

[39]. Ong, S. T., C. K. Lee, and Z. Zainal. "Removal of basic and reactive dyes using ethylenediamine modified rice hull." Bioresource technology 98, no. 15 (2007): 2792-2799.

[40]. Walker, G. M., L. Hansen, J-A. Hanna, and S. J. Allen. "Kinetics of a reactive dye adsorption onto dolomitic sorbents." Water Research 37, no. 9 (2003): 2081-2089.

[41]. Ho, Yuh-Shan. "Review of second-order models for adsorption systems." Journal of hazardous materials 136, no. 3 (2006): 681-689.

[42]. Chuah, T. G., A. Jumasiah, I. Azni, S. Katayon, and SY Thomas Choong. "Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview." Desalination 175, no. 3 (2005): 305-316.

[43]. Hameed, B. H., D. K. Mahmoud, and A. L. Ahmad. "Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste." Journal of Hazardous Materials 158, no. 1 (2008): 65-72.

[44]. Hameed, B. H., and H. Hakimi. "Utilization of durian (Durio zibethinus Murray) peel as low cost sorbent for the removal of acid dye from aqueous solutions." Biochemical Engineering Journal 39, no. 2 (2008): 338-343.

[45]. Gong, Renmin, Youbin Jin, Fayang Chen, Jian Chen, and Zhili Liu. "Enhanced malachite green removal from aqueous solution by citric acid modified rice straw." Journal of hazardous materials 137, no. 2 (2006): 865-870.

[46]. Ho, Y. S., and G. McKay. "The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat." The Canadian Journal of Chemical Engineering 76, no. 4 (1998): 822-827.

[47]. Li, Yanzhong, Changjun Liu, Zhaokun Luan, Xianjia Peng, Chunlei Zhu, Zhaoyang Chen, Zhongguo Zhang, Jinghua Fan, and Zhiping Jia. "Phosphate removal from aqueous solutions using raw and activated red mud and fly ash." Journal of Hazardous Materials 137, no. 1 (2006): 374-383.

[48]. Ramakrishna, Konduru R., and T. Viraraghavan. "Use of slag for dye removal." Waste Management 17, no. 8 (1998): 483-488.

[49]. Rao, M., A. V. Parwate, and A. G. Bhole. "Removal of Cr 6+ and Ni 2+ from aqueous solution using bagasse and fly ash." Waste management 22, no. 7 (2002): 821-830.

[50]. Baek, Mi-Hwa, Christianah Olakitan Ijagbemi, O. Se-Jin, and Dong-Su Kim. "Removal of Malachite Green from aqueous solution using degreased coffee bean." Journal of hazardous materials 176, no. 1 (2010): 820-828.

[51]. Hameed, B. H., D. K. Mahmoud, and A. L. Ahmad. "Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste." Journal of Hazardous Materials 158, no. 1 (2008): 65-72.

[52]. Namasivayam, C., and Dyes Kavitha. "Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an

agricultural solid waste." Dyes and pigments 54, no. 1 (2002): 47-58.

[53]. Hameed, B. H., D. K. Mahmoud, and A. L. Ahmad. "Sorption equilibrium and kinetics of basic dye from aqueous solution using banana stalk waste." Journal of Hazardous Materials 158, no. 2 (2008): 499-506.

[54]. Baek, Mi-Hwa, Christianah Olakitan Ijagbemi, O. Se-Jin, and Dong-Su Kim. "Removal of Malachite Green from aqueous solution using degreased coffee bean." Journal of hazardous materials 176, no. 1 (2010): 820-828.

[55]. Alver, Erol, and Ayşegül Ü. Metin. "Anionic dye removal from aqueous solutions using modified zeolite: Adsorption kinetics and isotherm studies." Chemical Engineering Journal 200 (2012): 59-67.

[56]. Daraei, Hasti, Alok Mittal, Mohammad Noorisepehr, and Jyoti Mittal. "Separation of chromium from water samples using eggshell powder as a low-cost sorbent: Kinetic and thermodynamic studies." Desalination and Water Treatment 53, no. 1 (2015): 214-220.

[57]. Saeed, Asma, Mehwish Sharif, and Muhammad Iqbal. "Application potential of grapefruit peel as dye sorbent: kinetics, equilibrium and mechanism of crystal violet adsorption." Journal of Hazardous Materials 179, no. 1 (2010): 564-572.

[58]. Liu, Peng, and Liuxue Zhang. "Adsorption of dyes from aqueous solutions or suspensions with clay nano-adsorbents." Separation and Purification Technology 58, no. 1 (2007): 32-39.

[59]. Gürses, A., Ç. Doğar, M. Yalçın, M. Açıkyıldız, R. Bayrak, and S. Karaca. "The adsorption kinetics of the cationic dye, methylene blue, onto clay." Journal of Hazardous Materials 131, no. 1 (2006): 217-228.

[60]. Gong, Renmin, Youbin Jin, Fayang Chen, Jian Chen, and Zhili Liu. "Enhanced malachite green removal from aqueous solution by citric acid modified rice straw." Journal of hazardous materials 137, no. 2 (2006): 865-870.

[61]. Mohan, Dinesh, Kunwar P. Singh, Gurdeep Singh, and Kundan Kumar. "Removal of dyes from wastewater using flyash, a low-cost adsorbent." Industrial & engineering chemistry research 41, no. 15 (2002): 3688-3695.

[62]. Denizli, Adil, Mustafa Kocakulak, and Erhan Pişkin. "Bilirubin removal from human plasma in a packed-bed column system with dye-affinity microbeads." Journal of Chromatography B: Biomedical Sciences and Applications 707, no. 1 (1998): 25-31.

[63]. Mahmoodi, Niyaz Mohammad. "Equilibrium, kinetics, and thermodynamics of dye removal using alginate in binary systems." Journal of Chemical & Engineering Data 56, no. 6 (2011): 2802-2811.

[64]. Alver, Erol, and Ayşegül Ü. Metin. "Anionic dye removal from aqueous solutions using modified zeolite: Adsorption kinetics and isotherm studies." Chemical Engineering Journal 200 (2012): 59-67.

[65]. Gupta, Vinod Kumar, Rajeev Jain, and Shaily Varshney. "Removal of Reactofix golden yellow 3 RFN from aqueous solution using wheat husk—an agricultural waste." Journal of Hazardous Materials 142, no. 1 (2007): 443-448.

[66]. Hameed, B. H., and H. Hakimi. "Utilization of durian (Durio zibethinus Murray) peel as low cost sorbent for the removal of acid dye from aqueous solutions." Biochemical Engineering Journal 39, no. 2 (2008): 338-343.

[67]. Al-Degs, Yahya S., Musa I. El-Barghouthi, Amjad H. El-Sheikh, and Gavin M. Walker. "Effect of solution pH, ionic strength, and temperature on adsorption behavior of reactive dyes on activated carbon." Dyes and pigments 77, no. 1 (2008): 16-23.

[68]. Ertaş, Murat, Bilal Acemioğlu, M. Hakkı Alma, and Mustafa Usta. "Removal of methylene blue from aqueous solution using cotton stalk, cotton waste and cotton dust." Journal of Hazardous Materials 183, no. 1 (2010): 421-427.

[69]. Gupta, V. K., Imran Ali, V. K. Saini, Tom Van Gerven, Bart Van der Bruggen, and Carlo Vandecasteele. "Removal of dyes from wastewater using bottom ash." Industrial & engineering chemistry research 44, no. 10 (2005): 3655-3664.

[70]. Tunc, Özlem, Hacer Tanacı, and Zümriye Aksu. "Potential use of cotton plant wastes for the removal of Remazol Black B reactive dye." Journal of Hazardous Materials 163, no. 1 (2009): 187-198.

[71]. Allen, Stephen J., Quan Gan, Ronan Matthews, and Pauline A. Johnson. "Comparison of optimised isotherm models for basic dye adsorption by kudzu." Bioresource Technology 88, no. 2 (2003): 143-152.

[72]. Crini, Grégorio. "Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin

polymer."Dyes and Pigments 77, no. 2 (2008): 415-426.

[73]. Annadurai, Gurusamy, Lai Yi Ling, and Jiunn-Fwu Lee. "Adsorption of reactive dye from an aqueous solution by chitosan: isotherm, kinetic and thermodynamic analysis." Journal of hazardous materials 152, no. 1 (2008): 337-346.

[74]. Gong, Renmin, Yi Ding, Mei Li, Chao Yang, Huijun Liu, and Yingzhi Sun. "Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution." Dyes and Pigments 64, no. 3 (2005): 187-192.

[75]. Ferrero, Franco. "Dye removal by low cost adsorbents: Hazelnut shells in comparison with wood sawdust." Journal of Hazardous Materials 142, no. 1 (2007): 144-152.

[76]. Kyzas, George Z., and Nikolaos K. Lazaridis. "Reactive and basic dyes removal by sorption onto chitosan derivatives." Journal of Colloid and Interface Science 331, no. 1 (2009): 32-39.

[77]. Demirbas, Ayhan. "Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review." Journal of hazardous materials 167, no. 1 (2009): 1-9.

[78]. Mane, Venkat S., Indra Deo Mall, and Vimal Chandra Srivastava. "Kinetic and equilibrium isotherm studies for the adsorptive removal of Brilliant Green dye from aqueous solution by rice husk ash." Journal of Environmental Management 84, no. 4 (2007): 390-400.

[79]. Mall, Indra Deo, Vimal Chandra Srivastava, Nitin Kumar Agarwal, and Indra Mani Mishra. "Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses."Chemosphere 61, no. 4 (2005): 492-501.

[80]. Walker, G. M., L. Hansen, J-A. Hanna, and S. J. Allen. "Kinetics of a reactive dye adsorption onto dolomitic sorbents." Water Research 37, no. 9 (2003): 2081-2089.

[81]. Namasivayam, C., and Dyes Kavitha. "Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste." Dyes and pigments 54, no. 1 (2002): 47-58.

[82]. Ahmad, A. A., B. H. Hameed, and N. Aziz. "Adsorption of direct dye on palm ash: Kinetic and equilibrium modeling." Journal of Hazardous Materials 141, no. 1 (2007): 70-76.

[83]. Ho, Y. S., and G. McKay. "A two-stage batch sorption optimized design for dye removal to minimize contact time." Process Safety and Environmental Protection 76, no. 4 (1998): 313-318.

[84]. Yuh-Shan, Ho. "Citation review of Lagergren kinetic rate equation on adsorption reactions." Scientometrics 59, no. 1 (2004): 171-177.

[85]. Inbaraj, B. Stephen, and N. Sulochana. "Basic dye adsorption on a low cost carbonaceous sorbent-kinetic and equilibrium studies." (2002).

[86]. Alver, Erol, and Ayşegül Ü. Metin. "Anionic dye removal from aqueous solutions using modified zeolite: Adsorption kinetics and isotherm studies."Chemical Engineering Journal 200 (2012): 59-67.

[87]. Malik, P. Kumar. "Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36." Dyes and pigments 56, no. 3 (2003): 239-249.

[88]. Wu, Feng-Chin, Ru-Ling Tseng, and Ruey-Shin Juang. "Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan." Water Research 35, no. 3 (2001): 613-618.

[89]. Gong, Renmin, Mei Li, Chao Yang, Yingzhi Sun, and Jian Chen. "Removal of cationic dyes from aqueous solution by adsorption on peanut hull." Journal of Hazardous Materials 121, no. 1 (2005): 247-250.

[90]. Ho, Y. S., and G. McKay. "The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat." The Canadian Journal of Chemical Engineering 76, no. 4 (1998): 822-827. Hameed, B. H., D. K. Mahmoud, and A. L. Ahmad. "Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste." Journal of Hazardous Materials 158, no. 1 (2008): 65-72.

[91]. Lin, Su-Hsia, and Ruey-Shin Juang. "Heavy metal removal from water by sorption using surfactant-modified montmorillonite." Journal of Hazardous Materials 92, no. 3 (2002): 315-326.

[92]. Barka, Noureddine, Mohammed Abdennouri, and Mohammed EL Makhfouk. "Removal of Methylene Blue and Eriochrome Black T from aqueous solutions by biosorption on Scolymus hispanicus L.: Kinetics, equilibrium and thermodynamics." Journal of the Taiwan Institute of Chemical Engineers42, no. 2 (2011): 320-326.

[93]. Oliveira, Leandro S., Adriana S. Franca, Thiago M. Alves, and Sonia DF Rocha. "Evaluation of untreated coffee husks as potential biosorbents for treatment of dye contaminated waters." Journal of Hazardous Materials 155, no. 3 (2008): 507-512.

[94]. Crini, Gregorio, and Pierre-Marie Badot. "Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: a review of recent literature." Progress in polymer science 33, no. 4 (2008): 399-447.

[95]. Belala, Zohra, Mejdi Jeguirim, Meriem Belhachemi, Fatima Addoun, and Gwenaëlle Trouvé. "Biosorption of basic dye from aqueous solutions by Date Stones and Palm-Trees Waste: Kinetic, equilibrium and thermodynamic studies." Desalination 271, no. 1 (2011): 80-87.

[96]. Cestari, Antonio R., Eunice FS Vieira, Andréa MG Tavares, and Roy E. Bruns. "The removal of the indigo carmine dye from aqueous solutions using cross-linked chitosan—Evaluation of adsorption thermodynamics using a full factorial design." Journal of Hazardous Materials 153, no. 1 (2008): 566-574.

[97]. Çolak, Ferdağ, Necip Atar, and Asim Olgun. "Biosorption of acidic dyes from aqueous solution by Paenibacillus macerans: Kinetic, thermodynamic and equilibrium studies." Chemical Engineering Journal 150, no. 1 (2009): 122-130.

[98]. Khattri, S. D., and M. K. Singh. "Colour removal from synthetic dye wastewater using a bioadsorbent." Water, Air, and Soil Pollution 120, no. 3-4 (2000): 283-294.

[99]. Alver, Erol, and Ayşegül Ü. Metin. "Anionic dye removal from aqueous solutions using modified zeolite: Adsorption kinetics and isotherm studies."Chemical Engineering Journal 200 (2012): 59-67.

[100]. Tehrani-Bagha, A. R., H. Nikkar, N. M. Mahmoodi, M. Markazi, and F. M. Menger. "The sorption of cationic dyes onto kaolin: Kinetic, isotherm and thermodynamic studies." Desalination 266, no. 1 (2011): 274-280.

[101]. Zolgharnein, Javad, Zhaleh Adhami, Ali Shahmoradi, and S. Norollah Mousavi. "Optimization of removal of methylene blue by Platanus tree leaves using response surface methodology." Analytical Sciences 26, no. 1 (2010): 111-116.

[102]. Rajeshkannan, R., N. Rajamohan, and M. Rajasimman. "Removal of malachite green from aqueous solution by sorption on hydrilla verticillata biomass using response surface methodology." Frontiers of Chemical Engineering in China 3, no. 2 (2009): 146-154.

[103]. Aleboyeh, A., N. Daneshvar, and M. B. Kasiri. "Optimization of CI Acid Red 14 azo dye removal by electrocoagulation batch process with response surface methodology." Chemical Engineering and Processing: Process Intensification 47, no. 5 (2008): 827-832.

[104]. Sadeghi-Kiakhani, Mousa, Mokhtar Arami, and Kamaladin Gharanjig. "Preparation of chitosan-ethyl acrylate as a biopolymer adsorbent for basic dyes removal from colored solutions." Journal of Environmental Chemical Engineering 1, no. 3 (2013): 406-415.

[105]. Tovar-Gomez, Rigoberto, D. A. Rivera-Ramírez, Virginia Hernandez-Montoya, Adrian Bonilla-Petriciolet, C. J. Durán-Valle, and M. A. Montes-Morán. "Synergic adsorption in the simultaneous removal of acid blue 25 and heavy metals from water using a Ca (PO 3) 2-modified carbon." Journal of hazardous materials 199 (2012): 290-300.

[106]. Witek-Krowiak, Anna, Katarzyna Chojnacka, Daria Podstawczyk, Anna Dawiec, and Karol Pokomeda. "Application of response surface methodology and artificial neural network methods in modelling and optimization of biosorption process." Bioresource technology 160 (2014): 150-160.

[107]. Asfaram, Arash, Mehrorang Ghaedi, Alireza Goudarzi, and Maryam Rajabi. "Response surface methodology approach for optimization of simultaneous dye and metal ion ultrasound-assisted adsorption onto Mn doped Fe 3 O 4-NPs loaded on AC: kinetic and isothermal studies." Dalton Transactions 44, no. 33 (2015): 14707-14723.

[108]. Kousha, Masoud, Ehsan Daneshvar, Hakimeh Dopeikar, Delaram Taghavi, and Amit Bhatnagar. "Box–Behnken design optimization of Acid Black 1 dye biosorption by different brown macroalgae." Chemical Engineering Journal179 (2012): 158-168.

[109]. Dutta, Susmita, Aparupa Bhattacharyya, Arnab Ganguly, Samya Gupta, and Srabanti Basu. "Application of response surface methodology for preparation of low-cost adsorbent from citrus

fruit peel and for removal of methylene blue." Desalination 275, no. 1 (2011): 26-36.

[110]. Sadeghi-Kiakhani, Mousa, Mokhtar Arami, and Kamaladin Gharanjig. "Dye removal from colored-textile wastewater using chitosan-PPI dendrimer hybrid as a biopolymer: Optimization, kinetic, and isotherm studies." Journal of Applied Polymer Science 127, no. 4 (2013): 2607-2619.

[111]. Özacar, Mahmut, İ. Ayhan Şengil and Harun Türkmenler, "Equilibrium and kinetic data, and adsorption mechanism for adsorption of lead onto valonia tannin resin", Chemical Engineering Journal, 143:1, 2008, 32-42.

[112]. Özcan, Adnan, Adnan Özcana, A. Safa Özcana, Sibel Tunalib, Tamer Akarb and Ismail Kiranb, "Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper (II) ions onto seeds of Capsicum annuum", Journal of Hazardous Materials, 124:1, 2005, 200-208.

[113]. Adnan Özcana, Çiğdem Ömeroğlub, Yunus Erdoğanb and Safa Özcana A, "Modification of bentonite with a cationic surfactant: an adsorption study of textile dye Reactive Blue 19", Journal of hazardous materials, 140:1, 2007, 173-179.

[114]. Flavio A. Pavana, Eder C. Limaa, Silvio L.P. Diasa and Ana C. Mazzocatob, "Methylene blue biosorption from aqueous solutions by yellow passion fruit waste", Journal of hazardous materials, 150:3, 2008, 703-712.

[115]. Jeferson S. Piccin, Guilherme L. Dotto, Mery L. G. Vieira and Luiz A. A. Pinto, "Kinetics and mechanism of the food dye FD&C Red 40 adsorption onto chitosan", Journal of Chemical & Engineering Data, 56:10, 2011, 3759-3765.

[116]. Sirlei Rosab, Mauro C.M. Laranjeiraa, Humberto G. Rielab and Valfredo T. Fáverea, "Cross-linked quaternary chitosan as an adsorbent for the removal of the reactive dye from aqueous solutions", Journal of hazardous materials, 155:1, 2008, 253-260.

[117]. Saeed, Asma, Mehwish Sharif and Muhammad Iqbal, "Application potential of grapefruit peel as dye sorbent: kinetics, equilibrium and mechanism of crystal violet adsorption", Journal of Hazardous Materials, 179:1, 2010, 564-572.

[118]. Bedabrata Saha, Sourav Das, Jiban Saikia and Gopal Das, "Preferential and enhanced adsorption of different dyes on iron oxide nanoparticles: a comparative study", The Journal of Physical Chemistry C, 115:16, 2011, 8024-8033.

[119]. Frédéric Sauvage, Jean-David Decoppet, Min Zhang, Shaik Mohammed Zakeeruddin, Pascal Comte, Mohammad Nazeeruddin, Peng Wang and Michael Grätzel, "Effect of sensitizer adsorption temperature on the performance of dye-sensitized solar cells", Journal of the American Chemical Society, 133:24, 2011, 9304-9310.

[120]. SHENG GuoDong, YANG ShiTong, ZHAO DongLin, SHENG Jiang and WANG XiangKe, "Microscopic insights into the temperature-dependent adsorption of Eu (III) onto titanate nanotubes studied by FTIR, XPS, XAFS and batch technique", Chemical engineering journal, 217, 2013, 486-494.

[121]. Karuppuchamy, Subbian, Nonomura K, Yoshida T, Sugiura T and Minoura H, "Cathodic electrodeposition of oxide semiconductor thin films and their application to dye-sensitized solar cells", Solid State Ionics, 151, no. 1, 2002, 19-27.

[122]. Jaheon Kim, In-Sun Jung , Soo-Young Kim, Eunsung Lee, Jin-Koo Kang, Shigeru Sakamoto, Kentaro Yamaguchi and Kimoon Kim, "New cucurbituril homologues: syntheses, isolation, characterization, and X-ray crystal structures of cucurbit [n] uril (n= 5, 7, and 8)", Journal of the American Chemical Society, 122:3, 2000, 540-541.

[123]. Michal Kruk, Mietek Jaroniec, Ji Man Kim and Ryong Ryoo, "Characterization of highly ordered MCM-41 silicas using X-ray diffraction and nitrogen adsorption", Langmuir, 15:16, 1999, 5279-5284.

[124]. Michal Kruk, Mietek Jaroniec, Yasuhiro Sakamoto, Osamu Terasaki, Ryong Ryoo and Chang Hyun Ko, "Determination of pore size and pore wall structure of MCM-41 by using nitrogen adsorption, transmission electron microscopy, and X-ray diffraction", The Journal of Physical Chemistry B, 104:2, 2000, 292-301.

[125]. Kruk, Michal, Mietek Jaroniec and Abdelhamid Sayari, "Relations between pore structure parameters and their implications for characterization of MCM-41 using gas adsorption and X-ray diffraction", Chemistry of materials, 11:2, 1999, 492-500.

[126]. Brandon J. Lafferty, Matthew Ginder-Vogel, Mengqiang Zhu, Kenneth J. T. Livi and Donald L. Sparks, "Arsenite oxidation by a poorly crystalline manganese-oxide 2. Results from X-ray absorption spectroscopy and X-ray

diffraction", Environmental science & technology, 44:22, 2010, 8467-8472.

[127]. Na Lu, Xie Quan, JingYuan Li, Shuo Chen, HongTao Yu and GuoHua Chen, "Fabrication of boron-doped TiO2 nanotube array electrode and investigation of its photoelectrochemical capability", The Journal of Physical Chemistry C, 111:32 2007, 11836-11842.

[128]. Xujie Lü,Xinliang Mou,Jianjun Wu,Dingwen Zhang, Linlin Zhang, Fuqiang Huang, Fangfang Xu and Sumei Huang, "Improved Performance Dye Sensitized Solar Cells Using Nb Doped TiO2 Electrodes: Efficient Electron Injection and Transfer", Advanced Functional Materials, 20:3, 2010, 509-515.

[129]. Luca, Vittorio, Samitha Djajanti and Russell F. Howe, "Structural and electronic properties of sol-gel titanium oxides studied by X-ray absorption spectroscopy", The Journal of Physical Chemistry B, 102:52, 1998, 10650-10657.

[130]. Liang Lva, Jing Hea, Min Weia, D.G. Evansa, Xue Duan, "Uptake of chloride ion from aqueous solution by calcined layered double hydroxides: equilibrium and kinetic studies", Water Research, 40:4, 2006, 735-743.

[131]. Gupta V.K and Rastogi A, “Biosorption of SCB dye from aqueous solutions by green algae spirogyra species: Kinetics and equilibrium studies”, Journal of Hazardous Materials, 152: 2008, 407–414.

[132]. Flavio A. Pavan, Ana C. Mazzocato, Rosangela A. Jacques, Silvio L.P. Dias, “Ponkan peel A potential biosorbent for removal of Pb(II) ions from aqueous solution”, Biochemical Engineering Journal, 40: 2008, 357–362.

[133]. Ruhan Altun Anayurt, Ahmet Sari, Mustafa Tuzen, “Equilibrium, thermodynamic and kinetic studies on biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (lactarius scrobiculatus) biomass”, Chemical Engineering Journal, 151: 2009,255–261.

[134]. Lijuan Wang and Jian Li, "Removal of methylene blue from aqueous solution by adsorption onto crofton weed stalk", Bioresources, 8:2, 2013, 2521 - 2536