Modeling of Competitive Ultrasonic Assisted Removal of the Crystal Violet and Aura mineO using MWCNTs Functionalized by N-(3-nitrobenzylidene)-N'-trimethoxysilylpropyl-ethane-1,2-diamine: Equilibrium, Kinetics and Thermodynamic Study

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ABSTRACT

In this study, adsorbent was synthesized by covalently anchoring N-(3-nitro-benzylidene)-N-trimethoxysilylpropyl-ethane-1, 2-diamine onto multi-walled carbon nanotubes (NBATSPED-MWCNTs). This novel material was characterized by different techniques such as XRD, SEM and FT-IR.Subsequently, it was used for the ultrasound-assisted removal of Aura mine O(AO) and Crystal violet (CV) from aqueous solutions was investigated. The dependency of removal percentages to variables such as pH, initial dyes concentration,adsorbent dosage, sonication time on the removal percentages of AO and CV were simultaneously investigated by central composite design (CCD) under response surface methodology (RSM). It was shown that the adsorption of AO and CV follows the pseudo-second-order rate equation, while the Langmuir model explains equilibrium data. Isotherms had also been used to obtain the thermodynamic parameters such as free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of adsorption. The negative value of $\Delta G°$ indicates the feasibility and spontaneity of the adsorption process. The positive $\Delta H°$ suggests the endothermic nature of the adsorption. The positive values of ΔS_0 reflect the affinity of multi-walled carbon nanotubes functionalized towards CV and AO. A small amount of the adsorbent was able to remove more than 99.20% of both dyes rapidly with high adsorption capacity in binary-component system (69.36 mgg^{-1} and 120.65mg g^{-1}for AO and CV respectively).

Keywords: multi-walled carbon nanotubes, Response surface methodology, Ultrasound-assisted dye removal, Crystal Violet, Aura mine O.

INTRODUCTION

The colored dye effluents are considered to be highly toxic to the aquatic biota and affect the symbiotic process by disturbing the natural equilibrium by reducing photosynthetic activity and primary production due to the colorization of the water[1, 2]. Synthetic colors are widely used in food

industries, while some of them may generate hazards and problem to human health at excess level[3-5]. Colors and dyes hinder from light penetration and lead to production of carcinogenic and mutagenesis hazards[6]. These problems make emergency to design and develop new protocol to treat them and achieve a safe and clean media[7]. Auramine O (AO) and its hydrochloride salt are used in the coloring of paper, textiles and leather; also as food dye[8]. International Agency for Research on Cancer included

AO is sufficient evidence of carcinogenicity in experimental animals due to its bio-transformation to reactive species in target organs of both rats and humans[9]. AO, and its hydrochloride salts are used for coloring paper, textiles and leather[10]. International Agency for Research on Cancer (IARC) expressed more evidence of carcinogenicity ability of AO among chemicals related to its bio-transformation to reactive species in target organs of rats and humans[11, 12].

As a typical cationic dye, crystal violet (CV) belongs to the triphenylmethane group, which is widely applied in coloring paper, temporary hair colorant, and dyeing cottons and wools. CV may harm the body via inhalation, ingestion and skin contact. It has also been found to cause cancer and severe eye irritation to human beings[13-15]. Adsorption is one of the best and simple techniques for the removal of toxic and noxious impurities in comparison to other conventional protocols like chemical coagulation, ion exchange, electrolysis, biological treatments is related to advantages viz. lower waste, higher efficiency and simple and mild operational conditions[16-18]. Adsorption techniques also have more efficiency in the removal of pollutants which are highly stable in biological degradation process through economically feasible mild pathways[19-21]. Of these methods, nanomaterial's based adsorbents is highly recommended for dyes pollutants removal[22-26]. The best figures of merit in multi component dyes systems removal are based on development of novel method that permits their accurate simultaneous determination in mixtures. The encounter difficulties are serious peaks overlapping that subsequently impossible their direct determination in mixture using general equation like Beer–Lambert[26-28].

Conventional and classical optimization protocol (one at a time) failed to give useful knowledge about the interaction between variables while requiring intensive labor and consuming long time because of requiring high number of experiments. Central composite design (CCD) under response surface methodology (RSM) can efficiently be applied for handling both variables involved and responses without suffering above-mentioned draw backs[29-31]. This approach enables researchers to make a suitable predicative model to apply for several factors even in the presence of complex interactions to describe responses and find the optimal conditions with less time elapsed[32-35]. In this work, MWCNT was modified with Schiff base-like structure following its reaction with N-(3-nitro-benzylidene)-N0-trimethoxysilylpropyl-ethane-1, 2-diamine (NBATSPED-MWCNT). A novel adsorbent followed by the characterization using different techniques such as Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). This adsorbent was used for the ultrasound-assisted removal of the CV and AO from aqueous solutions. The influences of variables such as sonication time, amount of adsorbent, initial CV and AO as well as their possible interactions were investigated and successfully optimized by central composite design (CCD) under response surface methodology (RSM). The adsorption kinetics and isotherms were also studied

EXPERIMENTAL

Materials and instruments

Auramine and Crystal violet are fully described in Table1. They were supplied from Merck (Darmstadt, Germany). The stock solution (100mgL^{-1}) of each dye was achieved following dissolution of 10 mg of which in100 mL double distilled water, separately and suitable dilute on was performed to obtain working solution with desired concentration, N-(3-(trimethoxysilyl)-propyl)ethylene diamine(TSPED) and 2-nitrobenzaldehyde (NBA) were purchased from Sigma-Aldrich. Multiwall carbon nanotubes (MWCNTs) were supplied from Riedel-de Hean (Hannover, Germany), and other reagents were used in analytical grade from Merck Company. The pH was adjusted and measured using pH/Ion meter model 686 (Metronome, Switzerland, Swiss). AO and CV concentrations were determined using UV–Vis spectrophotometer model V-530 (Jasco, Japan) at wave-lengths of 434 nm and 588 nm, respectively.

The ultrasonic bath with heating system (Techno-GAZ SPA Ultrasonic System, Italy) was used at frequency 60Hz and power 130W. The morphology of the NBATSPED-MWCNT was studied by scanning electron microscopy (SEM; HitachiS-4160). The FTIR spectra of compounds were recorded on aJASCO-680 instrument in the range of 400-4000 cm⁻¹ using KBr pellet with ratio 1: 100 for samples to KBr. X-ray diffraction (XRD) pattern was recorded by an automated Philips X'PertX-ray diffractometer with $Cu_{K\acute{a}}$ radiation (40 kV and 30 mA) for 2è values .The software Design-Expert® software Version. 7.0was used for experimental design analysis and their subsequent regression analysis.

Preparation of NBATSPED-MWCNT

At first step, trimethoxysilyl propylethy-lenediamine supported on MWCNT (NH₂-MWCNT) was synthesized by the reaction of 1.8 mL N-(3-(trimethoxysilyl)-propyl)ethylene diamine and 0.1 g MWCNT in 20 mL of dichloromethane under reflux at 40°C in the oil bath for 24. Then, the obtained solid was filtered, rinsed sequentially with ethanol and dried in an oven at 50°C.Then, 0.9 g of 2-nitrobenzaldehyde was added to the resulting substance in 20 mL of methanol and refluxed at 60°C in oil bath for 24 h. The product was filtered, washed with 50 mL of ethanol, distilled water and then dried in oven for 10 h for 50°C. In this way, N-(3-nitro-benzylidene)-N0-trimethoxysilylpropyl-ethane-1, 2-diamine supported on MWCNT (NBATSPED-MWCNT) was obtained as a new adsorbent. The steps for the synthesis of the adsorbent are presented in Scheme 1.

Ultrasound-assisted multi-component adsorption of AO and CV on to NBATSPED-MWCNT

A batch process using NBATSPED-MWCNT in presence of ultrasound was applied for binary adsorption of AO and CV, while all experiments were under taken in a cylindrical glass vessel by adding 0.032g of adsorbent to 50 mL of AO and CVat pH

5.0 as optimum value. The vessel was immersed in an ultrasonic bath for 4 min at room temperature and subsequently the solutions were centrifuged. Then, non-adsorbed dye contents were determined by using UV–Vis spectrophotometer set at wavelengths 434 and 584 nm for AO and CV, respectively.

Measurements of dye uptake

The dye concentrations were determined from calibration curve obtained at maximum wavelength over working concentration range. The efficiency of dyes removal was determined at different experimental conditions optimized using the CCD method. The experiments were also performed in the initial dye concentration range of 5-25mg L⁻¹to obtains adsorption isotherms. The removal percentage of each dye was calculated using the following equation[25]:

$$R\% = \frac{(C_\circ - C_t)}{C_\circ} \times 100 \qquad ...(1)$$

Where, C_e (mg L⁻¹) and C_t (mg L⁻¹)is the concentration of target at initial and after time t respectively[36].

$$q_e = \frac{(C_\circ - C_e)V}{W} \qquad ...(2)$$

where C_0 (mg L⁻¹)and C_e (mg L⁻¹)are the initial dye concentration and equilibrium dye concentration in aqueous solution, respectively, V (L) is the solution volume and W (g) is the adsorbent mass.

Central Composite Design (CCD)

Response Surface Methodology is a statistical method that uses experimental data obtained from specified experimental design to model and optimize any process in which response of interest is influenced by several variables[37,38]. Primarily, this optimization is done by following three major steps, viz., performing the statistically
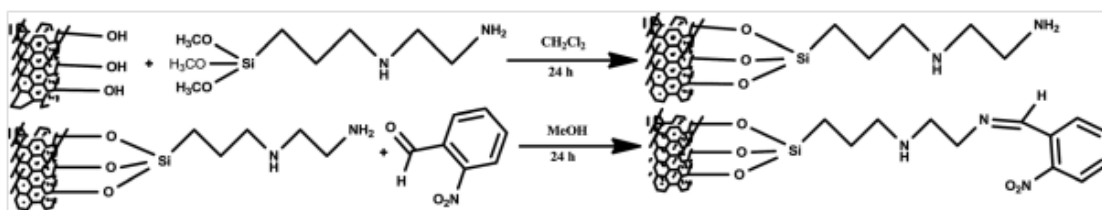
Scheme 1:

designed experiments, estimating the coefficients in a mathematical model, and predicting their responses followed by examining the adequacy of the model[39]. RSM helps to enumerate the relationships between output variables called responses(y) and input variables called factors ($X_i S$) [40].

$$y = f(X_1, X_2, X_3, ...X_n)$$
...(3)

CCD under RSM is suitable for fitting a quadratic surface to optimize the effective parameters and to investigate the contribution of variables and the interaction with minimum number of experiments[41]. Generally, the CCD consists of 2^n factorial runs with $2n$ axial runs and n_C central runs where n is the number of variables(n=5 in this work)[42], while the replication of central point gives a sense on numerical values of experimental errors and the data reproducibility. Thus, conducting 32 experiments permits the researchers for full study of all regions. Each experimental run was analyzed and the response was correlated with five input factors by using the following quadratic polynomial equation[29]:

$$y = \beta_\circ + \sum_{i=1}^{5} \beta_i X_i + \sum_{i=1}^{5}\sum_{j=1}^{5} \beta_j X_i X_j + \sum_{i=1}^{5} \beta_i X_i^2 + \varepsilon$$
...(4)

Where y is the predicted response (removal percentage); $X_i S$ are the independent variables AO and CV concentration, pH, amount of adsorbent and sonication time) that are known for each experimental run. The parameter β_0 is the model constant $\hat{a}_i$ is the linear coefficient; β_{ii} are the quadratic coefficients and β_{ij} are the cross-product coefficients and β is the residual term. The regression analysis is used to fit the equations for both responses to the experimental data and to estimate the statistical significance of the equation using the Design-Expert® software Version. 7.0software.

Obtain an optimal response. The first or second-order polynomial equations obtained according to the experimental responses as well as their subsequent fitting and the analysis of variance (ANOVA) help to estimate the main contribution of variables involved and their interaction[43]. The plot of three-dimensional graph leads to the generation of surface response applied for the prediction of best operating conditions according to *P*-values and *F*-values. In this work, the dependence of dyes removal percentages as responses on five factors such as the initial AO concentration, initial CV concentration, pH effect, amount of adsorbent and sonication time at five levels (Table2) was analyzed using the software Design-Expert® software according to 32 runs.

Desirability function (DF)

Desirability function (DF) creates a function for each individual response d_i leading to final output of global function (D), maximum value of which supports the achievement of optimum value[44]. The principle and application of desirability function for the best predication of real behavior of adsorption system was pointed out previously[35]. The desirability profiles indicate the predicted levels of variables, which produce the most desirable responses.

RESULTS AND DISCUSSION

Characterization of adsorbent

The FTIR spectrum of NBATSPED-MWCNTs (Fig 1), shows absorption peak at 1715 cm^{-1} corresponding to the stretching vibration of carbonyl groups. The broad peaks at 1086 cm^{-1} could be assigned to C–O stretching fromphenolic, alcoholic, etheric groups and to C–C bonds. The new peak appearing at ≈3400 cm^{-1} corresponds to OH stretching. This peak can be assigned to the hydroxyl group of moisture, or carboxylic groups. The aromatic C=C stretch is observed at ≈1459 cm^{-1}. The FT-IR spectrum of NH$_2$-MWCNT displays a new peak as a weak shoulderat2931 cm^{-1}, which corresponds to the stretching vibrations of C–H bonds in propyl group. After the addition of 2-nitrobenzaldehyde, the new peak appeared at 1635 cm^{-1} is related to C=N which indicates successful synthesis ofNBATSPED. Following the addition of NBA (Fig. 1), two peaks at 1324 and 1585 cm^{-1} are attributed to –NO$_2$groups which confirm again the success of this step[45] the morphological features of the samples studied by SEMare shown in (Fig. 2).After the surface modification with NBATSPED, the NBATSPED-functionalized MWCNTs became rough, larger and bundled[46]. The XRD pattern of the NBATSPED-MWCNTs (Fig.3) represents a peak at 25.961 (002) corresponding to the interlayer spacing of the nanotube. The peaks at 43.05(100),

53.92(004)and 78.5(100) correspond to diffractions and reflections from the carbon atoms[47] As seen, the highly crystalline nature of theMWCNTs after functionalizing with NBATSPED is confirmed, while the high intensity of peak at 53.49 (004) shows that there has been a small amount of material in amorphous state. Theobserved XRD pattern indicates that the prepared NBATSPEDMWCNT is well-synthesized.

Analysis of Central Composite Design

As it is seen from CCD(Table2), the effects of five dependent variables AO concentration (X_1),

CV concentration (X_2), pH (X_3), amount of adsorbent (X_4) and time of sonication (X_5) were investigated. 32 experiments and their corresponding responses are presented in Table 2. Analysis (ANOVA) was performed for the removal Percentageof variance of each dye by using Design-Expert® software Version. 7.0.(Table 2) the quality of the polynomial model equation was judged statistically by the coefficient of determination R^2 and its statistical significance was determined by *F*-test. *P*-values less than 0.05 are generally considered as a criterion for distinguishing statistically significant variables. However, Bonferroni test was applied to reduce alpha value to 0.01
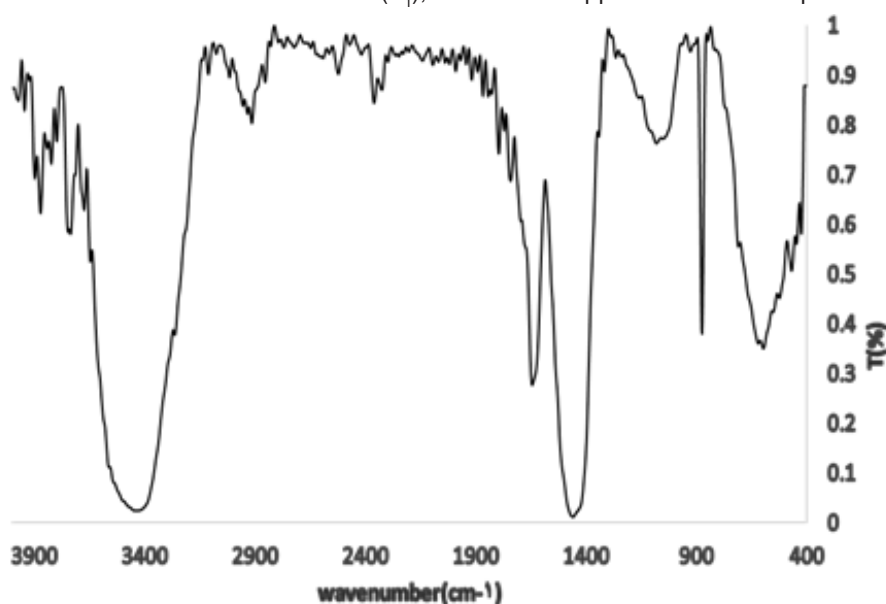

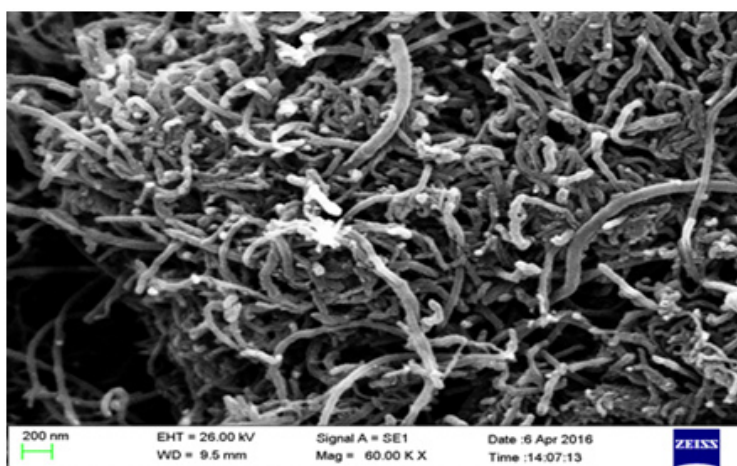**Fig.1: FT-IR, transmittance spectrum of the prepared NBATSPED-MWCNT**

Fig. 2: The SEM image of NBATSPED-MWCNT

which results in reducing the number of significant variables. As mentioned above, a *P*-value less than 0.01 (Bonferroni adjusted) indicates the statistical significance of each factor at 95% confidence level. Thus, the following predictive models describing the removal percentages of (AO) and (CV) dyes were obtained in terms of significant variables which satisfy the Bonferroni limit.

$$R\% AO = -184.15 - 7.10X_1 + 28.60X_2 + 71.77X_3 - 17611.10X_4 + 14.44X_5 - 0.23X_1X_2 - 1.61X_1X_3 + 295.14X_1X_4 - 0.34X_1X_5 - 1.77X_2X_3 + 20.54X_2X_4 - 2.52X_2X_5 + 626.01X_3X_4 - 2.40X_3X_5 + 2205.68X_4X_5 + (5)0.30X_1^2 - 0.10X_2^2 - 3.35X_3^2 + 8679.30X_4^2 + 0.25X_5^2$$

$$R\%CV = +7.64 + 12.58X_1 + 14.54X_2 + 23.92X_3 - 18369.80X_4 - 26.81X_5 - 0.32X_1X_2 - 1.21X_1X_3 + 50.88X_1X_4 - 1.13X_1X_5 - 0.84X_2X_3 + 119.50X_2X_4 - 0.86X_2X_5 + 913.10X_3X_4 + 2.80X_3X_5 + 2051.72X_4X_5 + 0.14X_1^2 - 0.10X_2^2 - 2.04X_3^2 + 53924.70X_4^2 + 0.16X_5^2 \qquad ...(6)$$

The plot of experimental *R*% values *versus* predicted ones indicated a good fit for both AO and CV (Fig.4). From ANOVA for the $R\%_{AO}$ and $R\%_{CV}$, the *P*-values for the lack of fits corresponding to AO and CV were obtained to be 0.16 and 0.33, respectively which prove the applicability of the predictive models. For both models, and adjusted were close to 1 confirming the goodness of the fit[13]. From Eq. (5), it is seen that the pH and its interaction with both AO and CV concentrations are significant which negatively affect $R\%_{AO}$. Another significant variable that positively affects $R\%_{AO}$ is amount of adsorbent. The trend in Eq. (6) corresponding to $R\%_{AO}$ is fairly similar to that of AO. However, CV concentration significantly affects the $R\%_{CV}$ negatively in linear and quadratic ways. Furthermore, the interaction of the pH with amount of adsorbent played significant role in $R\%_{AO}$ and $R\%_{CV}$.

Response surface plots

The 3D RSM surfaces corresponding to $R\%_{AO}$ and $R\%_{CV}$ were depicted and considered to optimize the significant factors and to give useful information about the possible interaction of variables. As also seen from Eqs.(5, 6), the effects of significant interaction terms on the curvature of the surfaces are observed as expected (Fig.5and 6). Fig (5a) shows the interaction of adsorbent dosage within initial dye concentration and their relation with removal percentage. It was seen that the removal percentage of dye decrease at higher initial dye
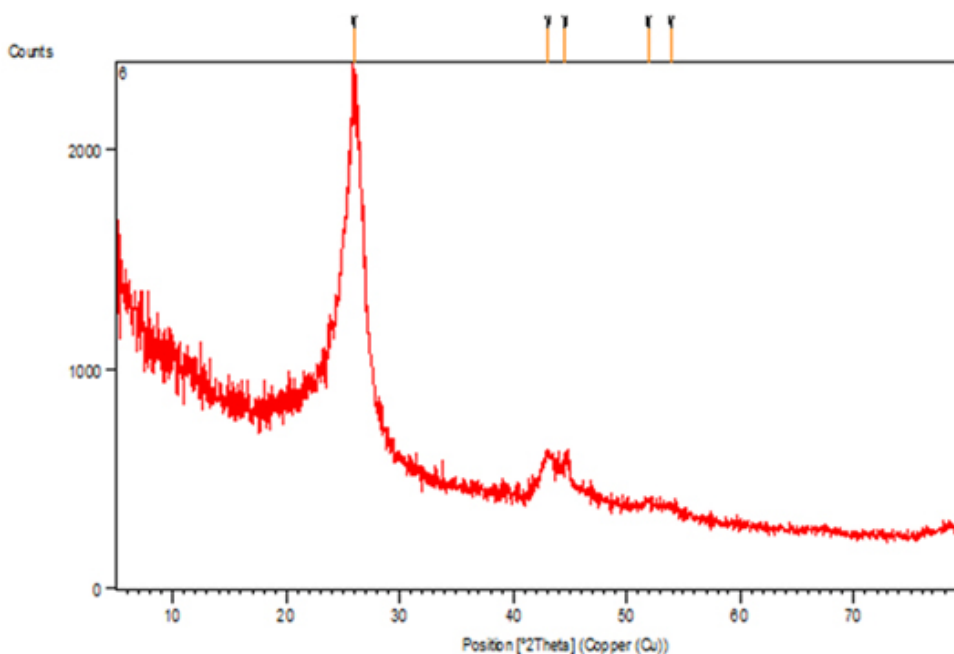
Fig. 3: XRD pattern of NBATSPED-MWCNT
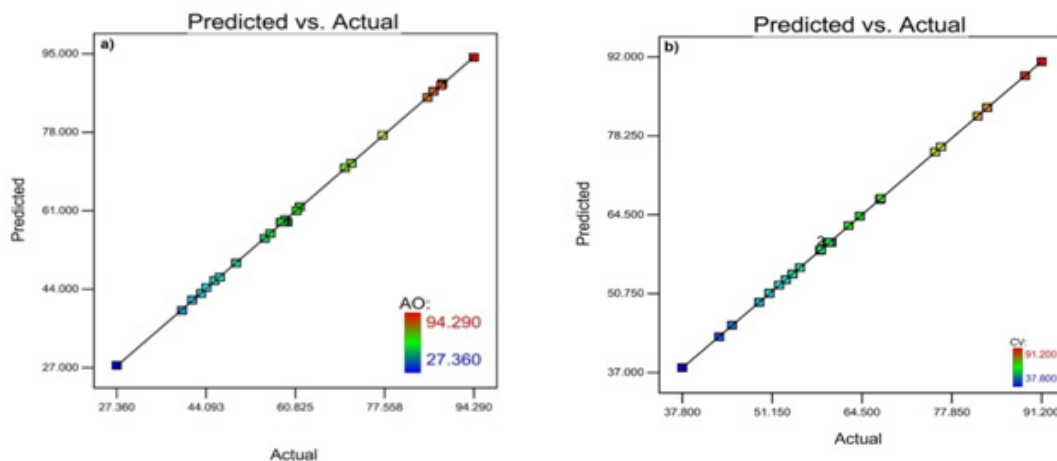
**Fig. 4: The experimental data versus
predicted data for removal of AO(a) and CV (b)**
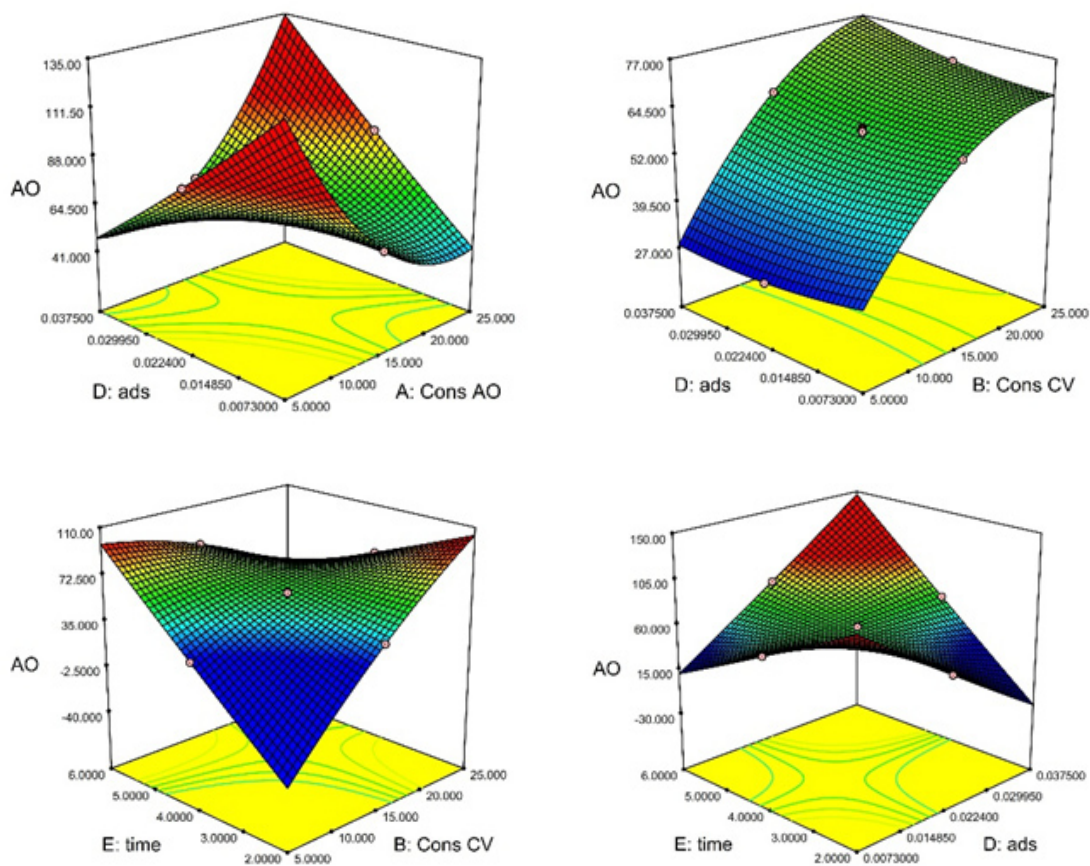
**Fig. 5: Response surfaces for the dyes removal: (a) initial (AO) concentration–adsorbent dosage
(b) initial (CV) concentration– adsorbent dosage; (c) initial (CV) concentration– sonication time,
(d) sonication time - adsorbent dosage**
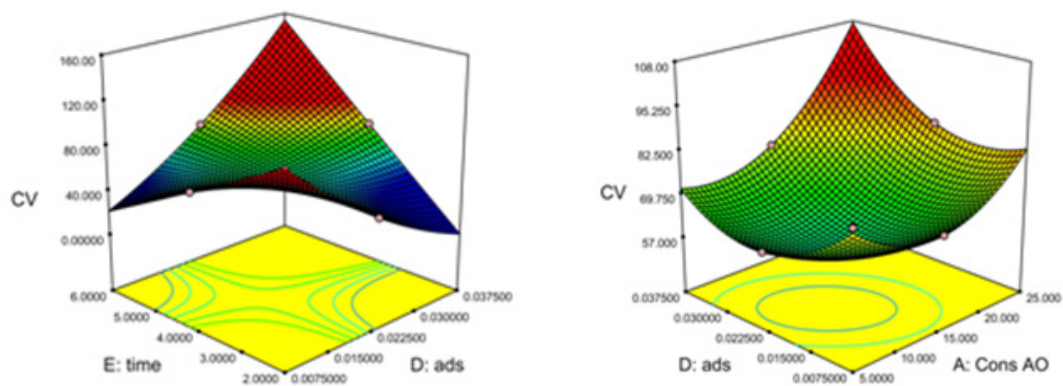
Fig. 6: Response surfaces for the dyes removal: (a) sonication time - adsorbent dosage(b) adsorbent dosage -initial (CV) concentration
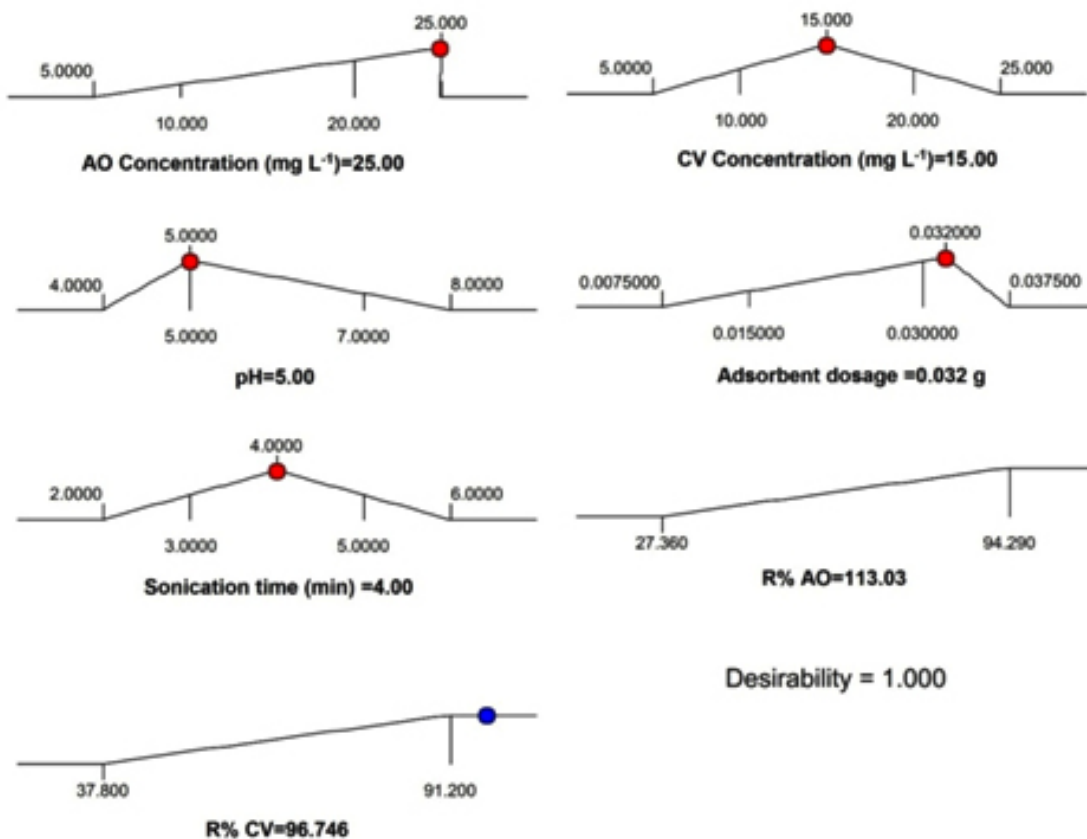
Fig. 7: Profiles for predicated values and desirability function for removal percentage of AO and CV. Dashed line indicates current values after optimization

Table 1: Properties of the dyes

Properties	Auramine O (AO)	Crystal violet(CV)
Color index number	41000	42.555
CAS number	2465-27-2	548-62-9
Chemical formula	$C_{17}H_{21}N_3.HCl$	$C_{25}H_{30}N_3Cl$
Molecular weight (g mol^{-1})	303.83	407.979
Maximum wavelength($\ddot{e}_{max,}$ nm)	434	584

concentration. This was also because of increase in the ratio of dye molecules to available adsorption surface area.

Fig (6a) shows the three dimensional response surface of the combined effect of weight and initial concentration on percentage removal with increase in initial concentration, removal decreases when weight of NBATSPED – MWCNT is kept constant. This is because at constant weight of NBATSPED – MWCNT when initial concentration of dye is increasing adsorbent gets saturated and it cannot adsorb further. Whereas with increase in weight of

NBATSPED – MWCNT percent removal increases monotonously. The reason is that when weight of NBATSPED – MWCNT is more, then the surface area available is also high, that increases the percentage removal.

The response surfaces plots Fig. 6b demonstrated the removal percentage dependency as a function of adsorbent dosage and contact time, the removal percentage increased with enhance in adsorbent dosage due to its high specific surface area and small particle size. At higher value probably due to increase in surface area and availability of more active adsorption sites the rate of adsorption significantly increased. At lower amount of NBATSPED – MWCNT, due to insufficiency of reactive sites and lower ratio of dye molecule to vacant site removal percentage significantly decreased.

Optimization of CCD by DF for extraction procedure

The profile for desirable option with predicted values in the Design-Expert software was used for the optimization of the process (Fig.7). The desirability in the range of 0.0 (undesirable) to 1.0 (very desirable) was used to obtain a global function (*D*) that is the base of optimization. Based on these calculations and desirability score of 1.0, maximum removal (100 and 97.00%for AO and CV, respectively)was obtained at optimum conditions as: 4 min for sonication time, 0.032g for adsorbent mass, 25 mgL^{-1} for AO and 15 mgL^{-1} for CV at pH 5.0. Five solutions with different amounts of ideal conditions were used to predict the optimum conditions for AO and CV dyes adsorption on to NBATSPED-MWCNT. The validity of the predicated responses at the optimized conditions was checked by performing duplicate experiments at similar conditions with RSD lower than 2% and removal percentage more than 97.5% in good agreement with the predicted value. This strong agreement proves that the predictive model found based on RSM is well applicable for describing the removal percentages of dyes studied against the variables involved.

Adsorption equilibrium study

Adsorption equilibrium isotherm is designed based on mathematical relation of the amount of adsorbed target per gram of adsorbent (q_e(mgg^{-1})) to the equilibrium non-adsorbed amount of dye in solution (C_e(mgL^{-1})) at fixed temperature[48,49]. Isotherm studies are divided to well-known models such as Langmuir, Freundlich, Temkin and Dubinin–Radushkevich based on well-known conditions. The Langmuir model is the most frequently employed model given by following equation[50]:

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$

... (7)

WhereC_e, $Q_m$andK_L are the concentration of adsorbate at equilibrium (mgL^{-1}), maximum

monolayer adsorption capacity (mgg^{-1}) and Langmuir constant (Lmg^{-1}), respectively.C_e/$q_e$was plotted against C_e where parameters such asQ_m, K_L, and R^2 were calculated based on the slope and intercept of such lines and displayed in Table4. The values of

K_a (the Langmuir adsorption constant (Lmg^{-1})) and Q_m(theoretical maximum adsorption capacity (mgg^{-1})) were obtained from the intercept and slope of the plot of C_e/q_e*ver.*C_e, respectively. The applicability of Langmuir modelfor the interpretation of the

Table 2: Experimental factors and levels in the central composite design

Factors		Levels	Star point α = 2.0			
		Low (-1)	Central (0)	High(+1)	-α	+α
(X$_1$) AO Concentration (mg L^{-1})		10	15	20	5	25
(X$_2$) CV Concentration (mg L^{-1})		10	15	20	5	25
(X$_3$) pH 5.0		6.0	7.0	4.0	8.0	
(X$_4$) Adsorbent mass (g)		0.0150	0.0225	0.0300	0.0075	0.0375
(X$_5$) Sonication time (min)		3.0	4.0	5.0	2.0	6.0
Experiment	Factors					Response (R %)
	X$_1$	X$_2$	X$_3$	X$_4$	X$_5$	AO	CV

Experiment	X$_1$	X$_2$	X$_3$	X$_4$	X$_5$	AO	CV
1	20	10	5.0	0.03	5	94.290	81.700
2	15	15	6.0	0.0225	4	58.700	59.900
3	15	15	6.0	0.0225	4	58.130	59.800
4	15	15	6.0	0.0375	4	61.700	76.250
5	15	15	6.0	0.0225	4	58.120	59.700
6	15	15	6.0	0.0225	4	58.190	59.650
7	5	15	6.0	0.0225	4	88.350	62.530
8	15	15	6.0	0.0225	4	58.250	59.450
9	15	15	6.0	0.0075	4	58.900	67.300
10	15	15	6.0	0.0225	2	41.500	45.190
11	15	15	6.0	0.0225	4	59.350	59.610
12	15	25	6.0	0.0225	4	70.140	64.190
13	15	15	8.0	0.0225	4	45.690	52.190
14	15	15	6.0	0.0225	6	77.190	75.360
15	20	20	7.0	0.015	3	61.090	55.300
16	10	20	5.0	0.03	5	85.600	88.750
17	20	20	5.0	0.015	5	49.750	53.190
18	10	20	7.0	0.015	5	56.170	58.410
19	15	15	6.0	0.0225	4	58.910	59.800
20	25	15	6.0	0.0225	4	86.700	83.110
21	15	15	6.0	0.0225	4	58.650	59.390
22	10	20	7.0	0.03	3	55.120	58.310
23	15	15	6.0	0.0225	4	58.350	59.710
24	20	20	5.0	0.03	3	71.360	67.190
25	20	10	7.0	0.015	5	46.700	54.180
26	15	15	6.0	0.0225	4	58.600	59.950
27	15	5	6.0	0.0225	4	27.360	37.800
28	15	15	4.0	0.0225	4	44.190	50.750
29	20	10	7.0	0.03	3	43.190	49.250
30	10	10	7.0	0.03	5	88.190	91.200
31	10	10	5.0	0.015	3	39.620	43.280

Table 3: Analysis of variance (ANOVA) for R% of AO and CV

Source of variation	Df	AO				CV			
		Sum of square	Mean square	F-value	P-value	Sum of square	Mean square	F-value	P-value
Model	20	7566.696	378.3348	2120.349	< 0.0001	4707.829	235.3915	7234.8	< 0.0001
X_1	1	1.36125	1.36125	7.629024	0.020058	211.7682	211.7682	6508.734	< 0.0001
X_2	1	915.0642	915.0642	5128.409	< 0.0001	348.2161	348.2161	10702.48	< 0.0001
X_3	1	1.125	1.125	6.304979	0.030861	1.0368	1.0368	31.86624	0.000214
X_4	1	3.92	3.92	21.96935	0.000858	40.05125	40.05125	1230.983	< 0.0001
X_5	1	636.8881	636.8881	3569.392	< 0.0001	455.1145	455.1145	13988.03	< 0.0001
X_1X_2	1	105.844	105.844	593.195	< 0.0001	220.6379	220.6379	6781.348	< 0.0001
X_1X_3	1	32.00386	32.00386	179.3632	< 0.0001	124.7979	124.7979	3835.685	< 0.0001
X_1X_4	1	415.2922	415.2922	2327.474	< 0.0001	12.34141	12.34141	379.3154	< 0.0001
X_1X_5	1	9.567833	9.567833	53.62221	< 0.0001	108.7885	108.7885	3343.636	< 0.0001
X_2X_3	1	264.3373	264.3373	1481.459	< 0.0001	59.72312	59.72312	1835.601	< 0.0001
X_2X_4	1	2.010673	2.010673	11.26867	0.007280	68.13461	68.13461	2094.13	< 0.0001
X_2X_5	1	537.6057	537.6057	3012.971	< 0.0001	62.60296	62.60296	1924.113	< 0.0001
X_3X_4	1	74.73716	74.73716	418.8589	< 0.0001	158.9877	158.9877	4886.516	< 0.0001
X_3X_5	1	19.32401	19.32401	108.3	< 0.0001	26.58836	26.58836	817.198	< 0.0001
X_4X_5	1	927.8001	927.8001	5199.787	< 0.0001	802.7982	802.7982	24674.15	< 0.0001
X_1^2	1	1658.351	1658.351	9294.105	< 0.0001	338.2771	338.2771	10397.01	< 0.0001
X_2^2	1	179.414	179.414	1005.513	< 0.0001	145.6453	145.6453	4476.435	< 0.0001
X_3^2	1	350.1421	350.1421	1962.345	< 0.0001	130.0834	130.0834	3998.138	< 0.0001
X_4^2	1	7.4285	7.4285	41.63248	< 0.0001	286.7545	286.7545	8813.452	< 0.0001
X_5^2	1	1.939488	1.939488	10.86972	0.0080552	0.780627	0.780627	23.99273	0.000625
Residual	10	1.784304	0.17843			0.32536	0.032536		
Lack of Fit	1	0.365054	0.365054	2.314946	0.16246	0.03372	0.03372	1.040599	0.33432
Pure Error	9	1.41925	0.157694			0.29164	0.032404		
Cor Total	30	7568.48				4708.155			
Standard deviation			0.42241				0.18038		
Coefficient of variation			0.69725				0.29239		
PRESS			202.380				18.891		
R^2			0.99976				0.99993		
Adjusted R^2			0.99929				0.99979		
Predicted R^2			0.97326				0.99599		
Adequate precision			191.80				359.19		

**Table 4: Various isotherm constants and their correlation coefficients
calculated for the adsorption of AO and CV on toNBATSPED-MWCNT**

Dye		AO	CV
Amount of adsorbent		0.02 g	0.02 g
Isotherm	Parameters	Value	
Langmuir	Q_m (mg.g^{-1})	69.36	120.65
	K_a (L mg^{-1})	0.852	0.213
	$R2$	0.990	0.990
Freundlich	$1/n$	0.321	0.639
	K_F(L mg^{-1})	3.96	4.95
	$R2$	0.93	0.97
Temkin	B_1	15.36	30.28
	K_T(L mg^{-1})	10.36	5.39
	R^2	0.94	0.95
Dubinin-Radushkevich	Q_s (mg g^{-1})	55.23	70.19
	$B \times 10^{-7}$	-1	-1
	E	2272.72	2272.72
	R^2	0.96	0.93

**Table 5: Various Kinetic constants and their correlation coefficients
calculated for the adsorption of AO and CV onto NBATSPED-MWCNT**

Model	Parameters	AO (20 mg L^{-1})	CV (10 mg L^{-1})
pseudo-First-orderkinetic	k_1(min^{-1})	0.521	0.326
	q_e (calc) (mg g^{-1})	7.96	6.32
	R^2	0.82	0.90
pseudo-Second-orderkinetic	k_2 (min^{-1})	0.101	0.145
	q_e(calc) (mg g^{-1})	26.39	20.36
	R^2	0.984	0.993
Intraparticlediffusion	K_{diff}(mg g^{-1} min$^{-1/2}$)	3.69	2.56
	C (mg g^{-1})	6.23	4.26
	R^2	0.94	0.96
Elovich	β (g mg^{-1})	0.63	0.726
	α (mg g^{-1} min^{-1})	396.58	263.39
	R^2	0.86	0.92
$q_{e\,(exp)}$(mg g^{-1})		27.86	21.32

Dye		AO					CV			
Temperature (K)	288.15	308.15	318.15	328.15	338.15	288.15	308.15	318.15	328.15	338.15
$\Delta G°$(kj mol^{-1})	-5.137	-7.673	-9.792	-11.998	-11.02	-3.802	-4.643	-5.724	-6.313	-8.834
$\Delta H°$(kj mol^{-1})			43.216					29.15		
$\Delta S°$(j mol^{-1} k^{-1})			197.32					150.55		

experimental data over the whole concentration range is proven from high correlation coefficient at all adsorbent masses. The increase in the amount of adsorbent leads to significant enhancement in the actual amount of adsorbed dye. The parameters of Freundlich isotherm model such as K_F and the capacity of the adsorption were calculated from the intercept and slope of the linear plot of $\ln q_e$ *versus* $\ln C_e$, respectively[51]. The heat of the adsorption and the adsorbent–adsorbate interaction were evaluated by using Temkin isotherm model[52]. In this model, B is the Temkin constant related to heat of the adsorption (Jmol^{-1}), T is the absolute temperature(K), R is the universal gas constant(8.314Jmol^{-1} K^{-1}) and K is the equilibrium binding constant(Lmg^{-1}). D–R model was applied to estimate the porosity apparent free energy and the characteristic of adsorption[53]. In this model B (mol^2/Kj^2) is a constant related to the adsorption energy, Q_S(mgg^{-1}) is the theoretical saturation capacity and E is the Polanyi potential. The slope of the plot of $\ln q_e$ *versus* μ^2 gives B and its intercept yields the Q_S value. The linear fit between the plot of C_e/q_e *versus* C_e and calculated correlation coefficient (R^2) for Langmuir isotherm model shows that the dye removal isotherm can be better represented by Langmuir model (Table4). This confirms that the adsorption of AO and CV dyes takes place at specific homogeneous sites as a monolayer on to the NBATSPED-MWCNT surface.

Kinetic study

Adsorption of a solute by a solid in aqueous solution through complex stages[54] is strongly influenced by several parameters related to the state of the solid (generally with very heterogeneous reactive surface) and to physico- chemical conditions under which the adsorption occurred. The rate of dyes adsorption onto adsorbent was fitted to traditional models like, pseudo-first, second-order, intra-particle and Elovich models. The Lagergren pseudo-first order modeled scribed the adsorption kinetic data[55]. The Lagergren is commonly expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad \ldots(8)$$

Where, q_t and dq_t(mgg^{-1}) are the adsorption capacities at equilibrium and at time t, respectively. k_1 is the rate constant of the pseudo-first-order

adsorption(Lmin^{-1}). The log (q_e"q_t) *versus* t was plotted and the values of k$_1$ and q$_e$ were determined by using the slope and intercept of the line, respectively[56].

$$\log(q_e - q_t) = \log q_t - (\frac{k_1}{2.303})t \qquad \ldots(9)$$

The fact that the intercept is not equal to q$_e$ imply that there action is unlikely to follow the first-order[57]. The relationship between initial solute concentration and rate of adsorption is linear when pore diffusion limits the adsorption process. Therefore, it is necessary to fit experimental data to another model (Table5) such as pseudo-second order model[58], based on the following equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad \ldots(10)$$

Eq.(11) is integrated over the interval 0 to t for t and 0 to q$_t$ for q$_e$ to give

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \ldots(11)$$

As mentioned above, the plot of log (q_e-q_t) *versus* t does not show good results for entire sorption period, while the plot of t/q$_t$ *versus* t shows a straight line. The values of k_2 and equilibrium adsorption capacity q$_e$ were calculated from the intercept and slope of the plot of t/q *versus* t (Table5). The calculated q$_e$ values at different working conditions like various initial dyes concentrations and/or adsorbent masses were close to the experimental data and higher R^2 values corresponding to this model confirm its more suitability for the explanation of experimental data. This indicates that the pseudo-second-order kinetic model applies better for the adsorption of AO and CV system for the entire sorption period the intraparticle diffusion equation is given as[59]:

$$q_t = k_{dif} t^{1/2} + C \qquad \ldots(12)$$

Where k_{dif} is the intraparticle diffusion rate constant (mg/(g. min$^{1/2}$)) and C shows the boundary layer thickness. The linear form of Elovich model is generally expressed as[60]:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t$$

...(13)

The kinetic data from pseudo-first and pseudo-second-order adsorption kinetic models as well as the intraparticle diffusion and Elovich model are given in Table5. The linear plots of t/q_t *versus t* indicated a good agreement between the experimental and calculatedq_e values for different initial dyes concentrations. Furthermore, the correlation coefficients of the pseudo-second-order kinetic model ($R^2 > 0.99$) were greater than that of the pseudo-first-order model ($R^2 < 0.95$). As a result, the adsorption fits to the pseudo-second-order better than the pseudo-first-order kinetic model.

Theoretical approach

In this work we have modeled some parts of our systems based on works [61-197] and we will start a theoretical calculation for any further research in this area.

Thermodynamic studies

The thermodynamic parameters, the values of enthalpy (ΔH^0), and entropy (ΔS^0), and Gibbs free energy (ΔG^0), of the sorption are useful in defining whether the sorption reaction is endothermic or exothermic and spontaneity of the adsorption process[55]the adsorption standard free energy changes (ΔG^0) can be calculated according to[198]:

$$\Delta G^\circ = -RTLnK_\circ$$

...(14)

Where, R (8.314 Jmol^{-1} K^{-1}) is the ideal gas constant, and T (K) is the temperature. The negative values at different temperatures were due to the fact that the adsorption process is spontaneous. The value of decreased with an increase in temperature, indicated that the spontaneous nature of the adsorption of AO and CV dyes is inversely proportional to the temperature. The values of other parameters such as enthalpy change and entropy change may be determined from Van't Hoff equation[199]:

$$LnK = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

...(15)

The Thermodynamic parameters are listed in Table 6. A positive standard enthalpy change suggests that the interaction of AO and CV by NBATSPED-MWCNT isendothothermic,which supported by the incresing feasibility adsotption AO and CV with the increase in temperature towards NBATSPED-MWCNT.

Comparison of various adsorbent

The performance of the proposed method has been compared with other adsorbents (Table7). The adsorption capacity and contact time for our work are superior to other adsorbents to removal AO. The results indicated that the ultrasound-assisted removal method has are mark able ability to improve the efficiency of dyes removal. The ultrasonic-assisted enhancement of dye removal could be attributed to the high-pressure shock wave sand high speed micro jets during the violent collapse of cavitation bubbles.

CONCLUSION

It is observed from the present study that the NBATSPED-MWCNT under the sonication is an efficient, fast and sensitive adsorption method for the removal of AO and CV. The influences of experimental parameters on the dyes removal percentages were investigated by experimental design methodology (RSM). The adsorption characteristic was examined with the variations of pH, sonication time, NBATSPED-MWCNTdosage, initial AO and CV concentration. The removal of AO and CV from aqueous solutions in short time (4 min) is feasible with high removal percentage at optimum pH (5.0) which is neutral and is an advantage for the adsorption process. The equilibrium data were best described by the Langmuir model. The process kinetics can be success fully fitted with pseudo-second order model Thermodynamic constants were evaluated using equilibrium constants changing with temperature. The negative values of ΔG° indicate the spontaneity and positive values of ΔH° showed the endothermic nature of AO and CV sorption. The data and methodology presented in this paper might be useful for designing the adsorbent for the treatment of actual effluent. Furthermore, the results of this study encourage the researches and industries to use ultrasound devices for more efficient dye

adsorption. The optimized method was successfully applied to real wastewater samples.

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