Efficient adsorption of erythrosine and sunset yellow onto modified palladium nanoparticles with a 2-diamine compound: Application of multivariate technique

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Abstract

Multiwalled carbon nanotubes (MWCNTs) functionalized with (N-3-phenylallylidene)-N'-trimethoxysilylpropyl-ethane-1, 2-diamine (PATMSPEDA) were prepared and subsequently the MWCNTs-PATMSPEDA-Pd-NPs nanohybrids with high shape selectivity and high specific surface area have been prepared by single step synthesis of Pd nanoparticles (Pd-NPs) loaded on MWCNTs-PATMSPEDA. These materials were characterized by different techniques such as XRD, SEM, FT-IR and TGA-DTA and subsequently were used for the simultaneous ultrasound-assisted removal of erythrosine (ER) and sunset yellow (SY) dyes from aqueous solution. The influences of important variables such as initial dyes concentration, adsorbent dosage, pH and sonication time on the efficiency of ultrasound-assisted removal process were investigated by central composite design (CCD) and the optimization conditions were obtained 4.39 and 4.33 mg L⁻¹ of ER concentration, 11.76 and 11.90 mg L⁻¹ of SY concentration, 0.02 and 0.019 g adsorbent mass, 7.0 and 7.0 for pH value and 3.88 and 3.75 min sonication time for MWCNTs-PATMSPEDA and MWCNTs-PATMSPEDA-Pd-NPs, respectively. The artificial neural network (ANN) model was used for building up to construct an empirical model to predict the understudy dyes removal behavior onto these adsorbents and the obtained results have good agreement with experimental data. The absolute average deviations (AADs) of ER and SY dyes adsorption by MWCNTs-PATMSPEDA are 0.62% and 0.58%, and the determination coefficient (R²) values are 0.971 and 0.978, respectively. Also, the AADs of ER and SY dyes adsorption by MWCNTs-PATMSPEDA-Pd-NPs are 0.48% and 0.34%, and the R² values are 0.971 and 0.972, respectively. Finally, it was found that the equilibrium isotherm of adsorption process follows the Langmuir isotherm. From the Langmuir isotherm, maximum monolayer capacity (q_{max}) were obtained to 30.58 and 38.76 mg g⁻¹ and 55.25 and 59.17 mg g⁻¹ at optimum conditions for ER and SY removal onto MWCNTs-PATMSPEDA and MWCNTs-PATMSPEDA-Pd-NPs, respectively.

Keywords: Ultrasonic assisted removal, erythrosine, sunset yellow, palladium nanoparticles, artificial neural network, central composite design

1. Introduction

Organic dyes are widely found in effluents discharged from paper, textiles, leather, food, plastics and cosmetic industries. Industrial wastewater of dyes can lead to serious environmental and health problems due to their high toxicity, chemical stability, slow degradation, and potential carcinogenicity [1-3]. Among these contaminations, sunset yellow is one of azo dyes that are added to a wide range of industrial products consist of beverage, jams, jelly, soup and sauces [4, 5]. It should be avoided by anyone suffering from existing allergic (asthma or urticaria) and leads to the water bodies colored and creates aesthetic problem limits the reoxygenation capacity of the receiving water and cuts-off sunlight for entering in water [6] [7]. Also, erythrosine as a water-soluble xanthene's class of dyes widely used as colorant in food, textile, drug and cosmetics. In

large concentrations it causes various damages such as types of allergies, thyroid activities, carcinogenicity, DNA damage behavior and neurotoxicity in the humans and animals [8, 9]. The photochemical and biochemical degradation of the erythrosine is not recommended due to formation of toxic by-products [10]. Thus it is mandatory to treat dye bath effluents prior to discharge into the surrounding aquatic systems. Treatments method like adsorption, chemical precipitation, coagulation and membrane filtration can be used to decontaminate effluents [11-13]. Some of these methods have been proven to be inefficient and extremely expensive in controlling pollutants level in wastewaters. While, adsorption process is cheap, in situ, easy, fast and novel approaches for the decontaminate wastewaters [14-19]. The adsorption-based processes are interest to implement the most of these considerations and requirements [20, 21]. Therefore, search and design a novel adsorbent in this method is important. Multi-walled carbon nanotubes (MWCNTs) due to excellent mechanical, electrical and thermal properties have been the focused as adsorbent in adsorption process, while their relatively low specific area, selectivity and functional group in its surface [22, 23]. Therefore, it is essential to improve this disadvantage with functionalized of these with organic and inorganic materials. Among the organic modifiers, Schiff base like agents are be suitable for support of metal based nanoparticles and selective interaction with analytes [24, 25]. In addition, in inorganic modifiers, Pd based nanoparticles (NPs) have attracted great attention for wastewater treatment due to their high specific surface area, high ordered structure, and excellent mechanical/thermal strength [26]. Hence, the industrial applications of these nanoparticles are also hindered due to their high cost and limited resources. To overcome these problems, immobilizing low amount of these noble-metal nanoparticles with specific shape on MWCNTs as solid supports is regarded as an effective strategy [22]. Therefore, the industrial applications of these nanoparticles are also hindered due to their high cost and limited resources. To overcome these problems, immobilizing noble-metal nanoparticles with specific shape on MWCNTs as solid supports is regarded as an effective strategy [23, 26, 27]. In our work, we developed an efficient and facile route for the in situ growth of palladium nanoparticles (Pd-NPs) on MWCNTs by ascorbic acid as reducing agent and (N-3-phenylallylidene)-N'-trimethoxysilylpropyl-ethane-1, 2-diamine (PATMSPEDA) as the coupling linker. The as-prepared adsorbent was successfully applied to the simultaneous ultrasonic assisted removal of erythrosine (ER) and sunset yellow (SY) dyes from aquaes solution. MWCNT and its functionalized adsorption is a proven and much used technique because of the low energy and maintenance costs, the simplicity and the reliability [28]. There is less experience with adsorption using other adsorbents, than there is for MWCNT adsorption. An advantage of using other adsorbents is that they are more specific and remove other substances than MWCNT [29].

To achieve the optimal adsorption efficiency, the effect of dyes concentration, adsorbents mass, sonication time and pH on under study dyes removal was investigated with central composite design (CCD).

In this case, the use of ultrasound in synthesis of material and assisted of adsorption is a more efficient mixing method in system, compared to conventional methods of agitation [30, 31]. The ultrasound energy improves the mass transfer between the immiscible reactants, increases the chemical reaction rate yield and decreases the reaction time as well as energy consumption. Ultrasound waves are sound waves that are above normal human hearing range [12, 32]. Ultrasound is known to manifest its physical and chemical effect on a liquid-liquid and liquid-solid heterogeneous reaction system through cavitation bubbles [31, 33]. Performing reactions at non-optimized conditions may lead to use of more resources with lesser output. Hence, the recent efforts have been focusing on modeling and optimization of key process parameters. In this case, experimental optimization techniques are reported in detail to optimize various experimental parameters. It is therefore envisaged that the use of coupled CCD and desirability function (DF) to sweep a region of interest and select the optimal (or near optimal) settings for the adsorption process [12, 30]. The artificial neural network (ANN) model are employed as algorithms for solving problems of mapping, regression, modeling, multivariate data analysis, optimization, control classification, and chemical differentiation to predict the understudy dyes removal behavior onto these materials [34, 35]. Finally, the

equilibrium isotherm analyses involved in the degradation process were also discussed to find out the possibility of using this material for dyes removal [36].

2. Experimental

2.1. Instruments and Reagents

Chemical reagents including N-(3-(trimethoxysilyl)-propyl) ethylenediamine, MWCNT, acetonitrile, cinnamaldehyde, SY, ER, Na₂PdCl₄, HCl and sodium hydroxide (NaOH) without further purification were purchased from Merck company (Dermasdat, Germany) and their solutions were prepared by dissolving their appropriate amount in double distilled water. The pH (the pH of various solutions was adjusted using HCl and/or NaOH) was measured using pH/Ion meter model 686 (Metrohm, Switzerland, Swiss). Methyl orange and sunset yellow concentration was determined using Jasco UV-VIS spectrophotometer model V-530 (Jasco, Japan). Samples were characterized by SEM (SEM: KYKY-EM3200, Hitachi Company, China) under an acceleration voltage of 26 kV) and XRD (PW 1800, Philips, Germany). An ultrasonic bath (Tecno-GAZ SPA Ultra Sonic System, Parma, Italy) at 40 kHz of frequency and 130 W of power was used for ultrasound-assisted adsorption procedure. Other chemicals and equipment's were used according to previous publication [32, 36-41].

2.2. Preparation of MWCNT-PATMSPEDA-Pd-NPs

At first step, trimethoxysilylpropylethylene diamine functionalized on MWCNT (MWCNT-NH₂) was synthesized by the reaction of 2.0 mL N-(3-(trimethoxysilyl)-propyl) ethylenediamine and 0.2 g MWCNT in 20 mL of acetonitrile under reflux at 60 °C in the oil bath for 24 h. Then, the obtained solid was filtered, rinsed sequentially with ethanol and dried in an oven at 50 °C. Then, 0.9 g of cinnamaldehyde 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 at 50 °C. In this way, (N-3-phenylallylidene)-N'-trimethoxysilylpropyl-ethane-1, 2-diamine supported on MWCNT (MWCNT-PATMSPEDA) was obtained as a new adsorbent. In next step, the Pd nanoparticles loaded MWCNT-PATMSPEDA were synthesized in a one-step reduction process in an aqueous solution. In a typical preparation, a 300 µL aliquot of a 0.02 mol/L Na₂PdCl₄ aqueous solution was added into 50 mL of an aqueous solution containing 0.2 wt % of the soluble starch and sonicated for 1 h. Then, the mixture was placed in a sonication bath and kept at 80 °C for 1 h. Subsequently, 5 mL of a 0.4 mol/L ascorbic acid aqueous solution was added to the Pd-soluble starch solution under constant stirring and at the preset temperatures for 5 min. After about 1.0 h the solution turned brown, which indicated the initial formation of the Pd nanoparticles. The mixture was maintained at 80 °C for 3 h under sonication and the color of the reaction solution became dark brown. Appropriate aliquots of the Pd nanoparticles solution was mixed with MWCNT-PATMSPEDA in a large and open Erlenmeyer under sonication for up to 12 h. The MWCNT-PATMSPEDA-supported Pd nanoparticles were then filtered and extensively washed with double distilled water. The MWCNT-PATMSPEDA supported Pd nanoparticles were generally dried at 70 °C for 1 h. The steps for the synthesis of the adsorbent are presented in Fig. 1.

<Fig. 1>

2.3. Ultrasonic assisted adsorption experiments

The adsorption of ER and SY dyes onto MWCNT-PATMSPEDA and MWCNT-PATMSPEDA-Pd-NPs were performed according to experimental runs in the CCD matrix as follow: the pH of various solutions with different concentration of ER and SY dyes was adjusted using HCl and/or NaOH into a 50 ml Erlenmeyer flask while mixed thoroughly with specific amounts of adsorbents in ultrasonic bath at room temperature. At the end of the reaction

time, the sample solution was immediately centrifuged and the supernatant containing residual was analyzed by UV–Vis spectroscopy. Typically, the absorbance spectra of this dyes in single and binary solution (in concentration of 8 mg L⁻¹ for each dye) is shown in Fig. 2, as seen that in spectrum of this dyes are not overlap in binary system. Therefore, the removal percentage of this dyes was calculated in wavelength of 417 and 529 nm for SY and ER, respectively. The removal percentage of dyes (R%) at a given time and the amount dyes adsorbed after reaching the equilibrium (q_e (mg g⁻¹)) in above appearance wavelength were calculated from the following equations [37, 39]:

$$R\% = ((C_0 - C_t) / C_0) \times 100 \quad (1)$$

$$q_e = ((C_0 - C_e) \times V) / W \quad (2)$$

where C_0 is the initial dyes concentration (mg L⁻¹), C_e is the residual dyes concentration at equilibrium state (mg/L), C_t is the residual dyes concentration at time t , V is the volume of the solution (L) and W is the weight of the adsorbent (g) used.

<Fig. 2>

2.4. Central composite design (CCD)

CCD under response surface methodology applied to evaluate the influence of operating parameters like concentration of dyes, adsorbents mass, pH and sonication time as input parameters, while their influence on R% of dyes onto MWCNT-PATMSPEDA and MWCNT-PATMSPEDA-Pd-NPs were considered as a response was investigated and optimized. The input variables, their levels and responses were presented in Table 1. All experimental designs were executed randomly to minimize experimental errors precisely. Then, the analysis of variance ANOVA from Design Expert 7.0 software at 95% confidence level was used to investigate of contribution of main factors and their interactions.

Table 1

2.5. Artificial neural network (ANN)

The ANNs supplies a non-linear function mapping of a set of input variables into the corresponding network output variables, without the requirement of having to identify the actual mathematics form of the relation between the input and output data.

One type of feed forward neural network that has been used generally for the approximate functions is multilayer perceptron (MLP) [42]. The MLP neural networks consist of multiple layers of simple activation units named neurons that are arranged in such a way that each neuron in one layer is linked with each neuron in the next by weighted connections (see Fig. 1). Neurons are arranged in layers that make up the global architecture. The MLP neural networks are contained of one input layer, at least one hidden layer and an output layer. The number of neurons in the hidden layer play the role of intermediate variables, may be considered as a which might be either output from other neurons or input from external sources. Each neuron computes a sum of the weighted inputs and changes it by the following transfer function:

$$n_j = \frac{1}{1 + \exp(-x)} \quad (3)$$

Where n_j is the output of the j -the neuron and x is given by:

$$x = \sum_{i=1}^n w_{ij} p_i + b_j \quad (4)$$

Where w_{ij} represents the weights applied to the relationships from the i -th neurons in the previous layer to the j -th neurons, p_i is the output from the i -th neuron and b is a bias term. The MLP networks operate in the supervised learning mode. In the training algorithm, training data are given to the networks and the network iteratively adjusts relation weights w and biases b until the network predicted values match the real values acceptably. In the back propagation error (BPE) training algorithm, this adjustment is performed by comparing the real value t_{ij} and the predicted values a_{ij} of the network through calculation of the total sum of the square error (SSE) for the n data of the training dataset,

$$SSE = \sum_{i=1}^n (t_{ij} - a_{ij})^2 \quad (5)$$

2.5.1. Network training and selection of the best topology of network

As above mentioned, the most regular neural network technique in solving problems is MLP. The MLP learns the data pattern by means of algorithms known as “training”, these algorithms adjust weights of the neurons consistent with the error between the values of actual and target output where provide non-linear regression between inputs and outputs variables and are very expensive in identifying designs in complex data. One of the most essential of training algorithms is the back-propagation algorithm.

“Tansig” and “Purelin” are two transfer functions that used in the hidden layer and output layer, respectively. Furthermore, the best network structure is demonstrated using the back propagation algorithm of Levenberg–Marquardt (trainlm). In this procedure, the number of hidden layers is firstly considered one. Then, the number of neurons in the hidden layer varied one by one to make the desire objective functions outputs by means of the trial and error approach. This leaning is continued to get the number of neurons which leads to lowest deviation for the testing subset and presented as the best number of neurons in the hidden layer.

The mean square error (MSE), the average absolute deviation (AAD %) and coefficient of determination (R^2) values were given as follow:

$$MSE = \sum_{i=1}^N (\rho_i^{\text{exp}} - \rho_i^{\text{cal}})^2 \quad (6)$$

$$AAD(\%) = \frac{1}{N} \sum_{i=1}^N \left(\left| \frac{\rho_i^{\text{exp}} - \rho_i^{\text{cal}}}{\rho_i^{\text{exp}}} \right| \right) \quad (7)$$

$$R^2 = \frac{\sum_{i=1}^N (\rho_i^{\text{exp}} - \bar{\rho})^2 - \sum_{i=1}^N (\rho_i^{\text{exp}} - \rho_i^{\text{cal}})^2}{\sum_{i=1}^N (\rho_i^{\text{exp}} - \bar{\rho})^2} \quad (8)$$

ANN under MATLAB toolbox was used as an experimental model to study the condition of ultrasonic assisted adsorption of ER and SY dyes. The input parameters to the ANN model were identical to the factors considered in CCD approach, namely, pH, dyes concentration, sonication time and adsorbents mass. Finally, the outputs obtained from the ANN modeling were compared with the experimental data, and advantages were discussed.

3. Results and discussion

3.1. Characterization of adsorbents

The FTIR spectrum (Fig. 4a) confirmed the presence of functional groups in MWCNT, MWCNT-NH₂, MWCNT-PATMSPEDA and MWCNT-PATMSPEDA-Pd-NPs hybrids. The absorption peak at 300-3400 cm⁻¹ in all of samples is corresponding to the stretching hydroxyl vibration groups. The broad peaks at 1180 cm⁻¹ could be assigned to C–O stretching form and C–C bonds in all of samples. The aromatic C=C stretch is observed at ~ 1580 cm⁻¹ in all sample spectra. The FT-IR spectrum of MWCNT-NH₂ displays a new peak as a weak shoulder at 2931 cm⁻¹, which corresponds to the stretching vibrations of C–H bonds in propyl group that in other spectra functionalized sample was shown. After the addition of cinnamaldehyde, the new peak appeared at 1650 cm⁻¹ is related to C=N which indicates successful synthesis of MWCNT-PATMSPEDA, and also this peak was shown in MWCNT-PATMSPEDA-Pd-NPs. Finally, the appearance of a new band at 937 cm⁻¹ in the MWCNT-PATMSPEDA-Pd-NPs spectrum confirmed the presence of Pd-NPs in the hybrid.

Thermal analysis of MWCNT-PATMSPEDA-Pd-NPs (Fig. 4b) reveals small mass reduction following the increase in temperature from room temperature to 150 °C which is probably related to the removal of physically adsorbed water molecules. Low mass reduction within the temperature variation from 300 to 400 °C is related to the removal of N2 group from the PATMSPEDA and maximum sample weight loss over the temperature range of 450 to 800 °C is due to the degradation process of the grafted organic groups of PATMSPEDA-Pd-NPs on MWCNT²⁸.

<Fig. 4>

The XRD pattern (Fig. 5) taken from the MWCNT illustrates strong peaks at the angles (2θ) of 25.95°, 46° and 53° which indicate the reflection of carbon structure and diffractions of graphite index of the MWCNT. In addition, the other characteristic diffraction peaks of MWCNT-PATMSPEDA at 2θ of about 53.76° is a marker for the presence of other groups in PATMSPEDA. In the XRD pattern (Fig. 5) taken from the MWCNT-PATMSPEDA-Pd-NPs appearance of four peaks are characteristic of face center cubic (fcc) crystalline of Pd-NPs, corresponding with the planes (111), (200), (220) and (311) at 2θ 40.11°, 46.50°, 68.04° and 81.78° respectively. The average size of Pd-NPs was calculated by Debye-Scherrer formula. For calculation of Pd-NPs size, the (111) reflection of the Pd face center cubic structure around 2θ 40.04°. The calculated average particle size in this research is approximately 20 nm. The observed XRD peaks indicate that the prepared samples are well-synthesized.

<Fig. 5>

The morphological features of the prepared samples were studied using SEM analysis (Fig. 6). In the SEM image of pure MWCNTs (Fig. 6a) before the surface modification it appears to be smooth, homogeneous, tidy and approximately uniform size distribution. After the surface modification with PATMSPEDA, SEM image of MWCNT-PATMSPEDA (Fig. 6b) reveal that smooth surface of MWCNTs has become rough, increase in the size and bundled. This confirms that the reaction between PATMSPEDA and MWCNTs was occurred. In addition, SEM image of MWCNT-PATMSPEDA-Pd-NPs (Fig. 6c) reveal that the spherical nanoparticles corresponding to Pd nanoparticles deposited on MWCNT-PATMSPEDA.

<Fig. 6>

3.2. CCD analysis

After fitting the data obtained for each parameter with the experimental design matrix (Table 1) the adequacy of the CCD was tested by ANOVA (Table 2). ANOVA for MWCNT-PATMSPEDA shows good model F values of 311.41 and 97.20 for R%_{ER} and R%_{SY}, respectively, as well as, for MWCNT-PATMSPEDA-Pd-NPs shows good model F values of 549.99 and 34.59 for R%_{ER} and R%_{SY}, respectively. Low P values (<0.0001) for more terms that confirm well applicability of constructed models for correlating the R% of the dyes indicate that these parameters are

significant and should be included in the models. And also, the Lack of Fit F-value for MWCNT-PATMSPEDA was to be 0.1423 and 0.9103 for $R\%_{ER}$ and $R\%_{SY}$ models respectively, as well as, for MWCNT-PATMSPEDA-Pd-NPs was to be 0.5033 and 0.365 for $R\%_{ER}$ and $R\%_{SY}$ models, respectively. This P values explanatory not significant relative to the pure error. Moreover, Not-significant lack of fit is good and model is a fit for simultaneous removal of understudy dyes by these adsorbents. However, the P values lower than 0.05 for variable as significant model terms are used in response surface quadratic model as follow:

$$R\%_{ER} \text{ in presence of MWCNT-PATMSPEDA} = 85.66 - 1.55X_1 + 0.18X_2 + 0.16X_3 + 3.31X_4 + 0.86X_5 - 0.83X_1X_2 - 1.23X_1X_3 + 0.69X_1X_4 + 1.06X_2X_3 - 0.55X_2X_4 + 0.44X_2X_5 - 1.04X_3X_4 + 0.80X_3X_5 + 0.55X_4X_5 + 1.03X_2^2 + 1.98X_3^2 - 0.91X_4^2 - 1.51X_5^2 \quad (9)$$

$$R\%_{SY} \text{ in presence of MWCNT-PATMSPEDA-NPs} = 82.22 - 1.09X_1 + 2.93X_2 + 1.32X_3 + 4.48X_4 + 1.61X_5 - 4.07X_1X_3 - 1.82X_1X_4 - 2.33X_1X_5 + 0.72X_2X_3 - 3.45X_3X_4 - 2.05X_3X_5 - 0.99X_4X_5 + 1.36X_3^2 - 2.24X_4^2 - 1.85X_5^2 \quad (10)$$

$$R\%_{ER} \text{ in presence of MWCNT-PATMSPEDA} = 90.74 - 3.23X_1 - 1.94X_2 + 2.11X_3 + 4.68X_4 - 0.16X_5 - 2.80X_1X_2 + 1.73X_1X_3 + 3.41X_1X_4 + 2.98X_2X_3 + 2.10X_2X_4 - 2.15X_2X_5 - 3.19X_3X_4 + 3.02X_3X_5 + 2.42X_4X_5 \quad (11)$$

$$R\%_{SY} \text{ in presence of MWCNT-PATMSPEDA-NPs} = 92.16 - 1.08X_1 + 2.51X_2 + 1.06X_3 + 4.02X_4 + 0.94X_5 - 3.54X_1X_3 - 1.45X_1X_4 - 1.69X_1X_5 - 2.88X_3X_4 - 1.75X_3X_5 - 0.95X_4X_5 + 0.83X_2^2 - 2.16X_4^2 - 1.77X_5^2 \quad (12)$$

Analysis of variance of the final model for MWCNT-PATMSPEDA the determination coefficient R^2 (0.9954 and 0.9853), predicated R^2 (0.9846, and 0.9590) and the adjusted R^2 (0.9922 and 0.9752) were obtained for $R\%_{ER}$ and $R\%_{SY}$ models, respectively. Also, in the presence of MWCNT-PATMSPEDA-Pd-NPs determination coefficient R^2 (0.9974 and 0.9598), predicated R^2 (0.9920 and 0.8733) and the adjusted R^2 (0.9956 and 0.9320) were obtained for $R\%_{ER}$ and $R\%_{SY}$ models, respectively, which these data confirm the suitability of applied models. The Adeq precision ratios for the models predicting $R\%_{ER}$ and $R\%_{SY}$ in presence of MWCNT-PATMSPEDA were found to be 74.626 and 46.602 and in presence of MWCNT-PATMSPEDA-Pd-NPs were found to be 97.588 and 27.383, respectively, which also indicate the sufficiency of models for simultaneous removal of these dyes. The another convenient expression of Eqs. (9)– (12) was also expressed by comparing simultaneous removal percentage of dyes between experiment and model predicted values for each adsorbent (Fig. 7). According to these plots good agreement between experimental and calculated value of dyes adsorption data was found for tow adsorbent.

<Table 2.>

<Fig. 7>

3.3. Optimization condition from CCD model

From these predictive models, it is needed to find the best condition at which the responses are maximized. For MWCNT-PATMSPEDA adsorbent it was found to be 4.39 mg L⁻¹, 11.76 mg L⁻¹, 0.02 g, 7.0 and 3.88 min for the concentration of ER, concentration of SY, adsorbent mass, pH and sonication time, respectively. At this condition, the $R\%_{ER}$ and $R\%_{SY}$ were found to be 98.28 % and 96.22 %. Also, for MWCNT-PATMSPEDA-Pd-NPs adsorbent these values were obtained to be 4.33 mg L⁻¹, 11.90 mg L⁻¹, 0.019 g, 7.0 and 3.75 min, respectively. To make a test on the validity of the prediction of the model, the experiment corresponding to the optimum condition was run for three times and average removal percentages for under study dyes in presence of these adsorbent was high agreement with the predicted values.

3.4. 3D response surface and contour plots

The 3D response surface and plots contour were used to illustrate the combined effects and identify the major interactions between of variables on R% of understudy dyes in presence of understudy adsorbents. In this work, typically four 3D response surface and contour plots are shown in Fig. 8.

Typically, the effect of sonication time on R%_{ER} and R%_{SY} (Fig. 8 all of section) show that with enhancement of sonication time, R% of dyes for tow adsorbent were increased that strongly support high contribution of ultrasound power in mass transfer. Is mainly because of the fact that at the initial stage of adsorption the high number of vacant surface sites is good and reactive sites for the acceleration of dyes onto the adsorbent following well dispersion of tow adsorbent into solution by ultrasonic power.

Typically, pH influence on ER adsorption were studied at room temperature by varying the pH of binary solution from 5-9 (Fig. 8a), while the zero charge pH of this adsorbent was 7.5. As seen that at pH lower than 7.5 due main force are electrostatic repulsive force, which hinder from mass transfer and lead to reduce in removal percentage. At the pH 7.5, dye deprotonating and absence of significant positive charge on adsorbent lead to enhance in dye mass transfer and removal percentage. On the other hand, the stability of adsorbent by formation of neutral lipophilic compound strongly elevated. Therefore, the maximum R%_{ER} was observed at pH 7.5 and at pH higher than 7.5 decreases removal percentage was seen. At higher pH, hydroxide ion and anionic form of dye mainly compete with each other for adsorption onto reactive sites of adsorbent.

Typically, the effect of initial ER and SY dye concentration on R%_{SY and ER} (Fig. 8c-f) reveal that the R% of tow dyes decrease with increases in initial dyes concentration. On other hand, at lower dyes concentration, high surface area of vacant sites of adsorbents are available that lead to increasing the concentration gradient and rate of dyes diffusion to adsorbents.

Typically, the effect of amount of MWCNT-PATMSPEDA-Pd-NPs on the R%_{ER} (Fig. 8g-h) reveal that by increasing of the amount of MWCNT-PATMSPEDA-Pd-NPs due to greater surface area and availability of high adsorption sites R%_{ER} was increased. With high amount of MWCNT-PATMSPEDA-Pd-NPs, the number of dye molecule to the vacant site is low that leads to higher migration and diffusion of dye molecules to the MWCNT-PATMSPEDA-Pd-NPs surface. Further increase in the amount of the MWCNT-PATMSPEDA-Pd-NPs does not bring any considerable change in the adsorption.

<Fig. 8>

3.5. ANN analysis

In this research, the ANN scheme has been employed to compute the ER and SY dyes removal behavior onto MWCNTs-PATMSPEDA and MWCNTs-PATMSPEDA-Pd-NPs. The input parameters to the ANN model are pH, dyes concentration, sonication time and adsorbents mass and the output parameters are dyes removal.

The MLP is trained, validated, and tested with random 70%, 15%, and 15%, respectively. The possibility of over-training is a problem in the ANN and can be overcome by proper selection of the number of neurons in hidden layer. The performance of the network in training phase should increase with increasing the number of neuron, at the same time as the performance of the network in testing data phase lead to optimum value at an optimal number of hidden neurons. In this research, the absolute average deviation (AAD %) was chosen as a measure of the performance of the net. The net with one hidden layer and 15 neurons was used to predict the ER and SY dyes removal by MWCNTs-PATMSPEDA and leads to the best prediction in Fig. 9a. Besides, the net with one hidden layer and 10 neurons for predict the ER and SY dyes removal by MWCNTs-PATMSPEDA-Pd-NPs leads to the best prediction in Fig. 9b. Figs. 10a and 10b show the evolution of training, validation, and test errors as a function of the number of training epochs (based on early stopping approach).

<Fig. 9>

<Fig. 10>

The optimized neural network model was used to predict the ER and SY dyes removal by MWCNTs-PATMSPEDA. The comparison between the predictive values and the experimental values is carried out and shown in Fig. 11. The results of Figs. 11 a and b show good agreement between the predicted and the experimental values of the ER and SY dyes removal by MWCNTs-PATMSPEDA and the AADs values are 0.62% and 0.58%, and the R^2 values are 0.971 and 0.978, respectively.

Besides, the results of Figs. 11c and d show good agreement between the predicted and the experimental values of ER and SY dyes removal by MWCNTs-PATMSPEDA-Pd-NPs. The AADs of ER and SY dyes removal by MWCNTs-PATMSPEDA-Pd-NPs are 0.48% and 0.34%, and the R^2 values are 0.971 and 0.972, respectively.

Fig. 12 shows the error analysis of trained net over number of test for the ER and SY dyes removal by MWCNTs-PATMSPEDA and MWCNTs-PATMSPEDA-Pd-NPs. The determination of coefficients (R^2) obtained from CCD and ANN for each dye and adsorbent were compared (Table 3). According to the Table 3, it is seen that results obtained from CCD and ANN are in good agreement with experimental observations.

<Fig. 11>

<Fig. 12>

Table 3

3.6 Adsorption equilibrium study

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species between the adsorbent and liquid phase at equilibrium as a function of adsorbate concentration [37, 38]. The experimental data obtained in this work were fitted to four equilibrium adsorption isotherm models such as Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) in tow value of adsorbent mass of each dyes in presence of MWCNT-PATMSPEDA and MWCNT-PATMSPEDA-Pd-NPs adsorbent, while other parameter was constant at optimum conditions, and result are summarized in Table 4. In other hand, adsorption isotherms models were used to obtained useful information about mechanism and accuracy of our results, calculate the theoretical maximum adsorption capacity and tendency of adsorbent toward each adsorbate.

According to Table 4, for tow adsorbent mass and adsorbent type the lower correlation coefficient (R^2) of the Freundlich, Temkin and Dubinin-Radushkevich models in comparison to Langmuir model (~ 1), suggest that the removal process better modeled by monolayer compare to multilayer adsorption. This means that the adsorption of dyes takes place at specific homogeneous sites and as a mono-layer adsorption onto on the outer surface of MWCNT-PATMSPEDA and MWCNT-PATMSPEDA-Pd-NPs. As well as, can be seen that the in all of adsorbent dosage and dyes type the adsorption capacity due to the higher than surface area of MWCNT-PATMSPEDA-Pd-NPs than to MWCNT-PATMSPEDA is greater.

Table 4

3.7. Comparison of this adsorbent with literature

Comparison of performance of the proposed method and this adsorbent with other methods and some adsorbents are summarized in Table 5. Accordingly, the MWCNT-PATMSPEDA-Pd-NPs and MWCNT-PATMSPEDA are superior to all other applied adsorbent in term of satisfactory removal performance for ER and SY. The results indicated that the combination of ultrasound with MWCNT-PATMSPEDA-Pd-NPs and MWCNT-PATMSPEDA

causes accelerated of mass transfer rate in less contact time (<3.88 min), as well as coupled metallic nanoparticles with functionalized MWCNT cause the increase in the adsorption capacity.

Insert Table 5

4. Conclusion

In this work, multiwalled carbon nanotubes as low selective and surface area support was functionalized with (N-3-phenylallylidene)-N'-trimethoxysilylpropyl-ethane-1, 2-diamine to the creation of new adsorbent and subsequently was decorated with Pd nanoparticles for preparation of novel high surface area and selective adsorbent. These materials successfully were characterized by different techniques such as XRD, SEM, FT-IR and TGA-DTG and subsequently was used for the ultrasound-assisted removal of erythrosine and sunset yellow dyes. The influences of important variables such as initial dyes concentration, adsorbent dosage, pH and sonication time on the efficiency of removal process were investigated by central composite design. The artificial neural network model was used for building up to construct an empirical model and obtained results show that ANN model is a powerful tool for prediction of understudy dyes adsorption by MWCNTs-PATMSPEDA and MWCNTs-PATMSPEDA-Pd-NPs. Finally, it was found that the equilibrium of adsorption process follows the Langmuir isotherm. From the Langmuir isotherm, maximum monolayer capacity ($q_{\max}$) were obtained to be 30.58 and 38.76 mg g⁻¹ and 55.25 and 59.17 mg g⁻¹ at optimum conditions for ER and SY removal onto MWCNTs-PATMSPEDA and MWCNTs-PATMSPEDA-Pd-NPs, respectively.

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Table 1. The design matrix and the responses.

	MWCNT-PATMSPEDA							MWCNT-PATMSPEDA-Pd-NPs						
	X ₁	X ₂	X ₃	X ₄	X ₄	R% _{ER}	R% _{SY}	X ₁	X ₂	X ₃	X ₄	X ₄	R% _{ER}	R% _{SY}
1	6	10	6	0.02	3	82.28	60.71	6	10	6	0.02	3	89.50	80.71
2	4	8	7	0.02	4	89.41	85.36	4	8	7	0.02	4	95.41	95.36
3	6	10	6	0.03	5	90.41	93.59	6	10	6	0.03	5	96.41	98.49
4	6	10	6	0.03	3	89.14	83.70	6	10	6	0.03	3	94.62	93.70
5	8	8	7	0.02	4	85.70	81.70	8	8	7	0.02	4	91.70	91.70
6	10	6	8	0.02	5	80.21	71.20	10	6	8	0.02	5	86.21	81.20
7	10	10	8	0.03	5	89.19	74.49	10	10	8	0.03	5	95.19	84.49
8	10	6	8	0.02	3	79.04	76.20	10	6	8	0.02	3	85.04	86.20
9	8	8	7	0.02	2	77.73	72.81	8	8	7	0.02	2	83.92	82.81
10	8	4	7	0.02	4	89.54	81.28	8	4	7	0.02	4	95.54	91.28
11	8	8	7	0.02	4	85.58	81.56	8	8	7	0.02	4	91.58	91.56
12	10	10	6	0.02	3	80.12	73.90	10	10	6	0.02	3	86.12	83.90
13	6	6	8	0.03	3	87.51	85.20	6	6	8	0.03	3	93.51	95.20
14	8	8	7	0.02	4	85.91	81.91	8	8	7	0.02	4	91.91	91.91
15	8	12	7	0.02	4	90.21	94.90	8	12	7	0.02	4	96.21	100.0
16	10	6	8	0.03	5	89.21	68.20	10	6	8	0.03	5	95.21	78.20
17	10	10	6	0.02	5	79.19	81.14	10	10	6	0.02	5	85.19	91.14
18	8	8	7	0.03	4	88.61	83.21	8	8	7	0.03	4	94.61	93.21
19	6	10	8	0.03	5	94.91	94.41	6	10	8	0.03	5	99.98	100.0
20	6	6	8	0.02	5	85.66	82.36	6	6	8	0.02	5	91.66	92.36
21	6	6	6	0.03	3	90.56	77.01	6	6	6	0.03	3	96.56	87.01
22	8	8	7	0.02	4	86.01	81.12	8	8	7	0.02	4	92.01	91.12
23	10	6	6	0.02	5	81.19	75.91	10	6	6	0.02	5	87.19	85.91
24	8	8	5	0.02	4	93.81	81.92	8	8	5	0.02	4	99.28	91.92
25	8	8	7	0.01	4	75.63	64.19	8	8	7	0.01	4	81.63	74.19
26	10	6	8	0.03	3	85.17	77.51	10	6	8	0.03	3	91.17	87.51
27	8	8	7	0.02	6	81.69	77.69	8	8	7	0.02	6	87.69	87.69
28	6	10	8	0.02	3	89.21	83.09	6	10	8	0.02	3	95.21	93.09
29	10	6	6	0.03	5	93.20	84.20	10	6	6	0.03	5	99.20	94.20
30	6	6	6	0.03	5	90.81	85.51	6	6	6	0.03	5	96.81	95.51
31	6	6	8	0.03	5	91.21	85.70	6	6	8	0.03	5	97.21	95.70
32	6	6	6	0.02	3	83.60	55.60	6	6	6	0.02	3	89.60	65.60
33	10	10	8	0.02	3	80.15	80.94	10	10	8	0.02	3	86.15	90.94
34	10	10	8	0.03	3	83.90	81.17	10	10	8	0.03	3	89.90	91.17
35	6	10	8	0.03	3	89.87	88.23	6	10	8	0.03	3	95.87	98.23
36	10	10	8	0.02	5	83.60	77.60	10	10	8	0.02	5	89.60	87.60
37	10	6	6	0.02	3	82.91	71.19	10	6	6	0.02	3	88.91	81.19
38	8	8	7	0.02	4	85.25	81.31	8	8	7	0.02	4	91.25	91.31
39	10	10	6	0.03	5	89.69	91.08	10	10	6	0.03	5	95.69	97.80
40	8	8	7	0.02	4	85.31	86.05	8	8	7	0.02	4	91.31	96.05
41	6	10	8	0.02	5	91.76	90.56	6	10	8	0.02	5	97.76	96.30
42	6	10	6	0.02	5	83.81	75.20	6	10	6	0.02	5	89.81	85.20
43	6	6	6	0.02	5	81.10	68.56	6	6	6	0.02	5	87.10	78.56
44	8	8	7	0.02	4	85.40	81.31	8	8	7	0.02	4	91.40	91.31
45	6	6	8	0.02	3	84.71	77.61	6	6	8	0.02	3	90.71	87.61
46	12	8	7	0.02	4	83.19	78.19	12	8	7	0.02	4	89.19	88.19
47	8	8	7	0.02	4	85.90	81.98	8	8	7	0.02	4	91.90	91.98
48	10	6	6	0.03	3	92.79	85.40	10	6	6	0.03	3	98.79	95.40
49	10	10	6	0.03	3	87.56	87.47	10	10	6	0.03	3	93.56	97.47
50	8	8	9	0.02	4	93.50	86.20	8	8	9	0.02	4	99.50	96.20

Table 2. The results of ANOVA for the response surface quadratic model.

		MWCNT-PATMSPEDA								MWCNT-PATMSPEDA-Pd-NPs									
	R% _{ER}						R% _{SY}				R% _{ER}					R% _{SY}			
Source of Variation	DF	Sum of Squares	Mean Square	F Value	p-value Prob > F		Sum of Squares	Mean Square	F Value	p-value Prob > F	Sum of Squares	Mean Square	F Value	p-value Prob > F		Sum of Squares	Mean Square	F Value	p-value Prob > F
Model	20	1028.18	51.41	311.41	< 0.0001		3082.42	154.12	97.2	< 0.0001	993.23	49.66	549.99	< 0.0001		2271.99	113.6	34.59	< 0.0001
X ₁	1	95.7	95.7	579.69	< 0.0001		47.92	47.92	30.22	< 0.0001	94.99	94.99	1051.9	< 0.0001		46.85	46.85	14.27	0.0007
X ₂	1	1.31	1.31	7.96	0.0085		343.16	343.16	216.41	< 0.0001	1.23	1.23	13.64	0.0009		251.55	251.55	76.59	< 0.0001
X ₃	1	1	1	6.07	0.0199		69.85	69.85	44.05	< 0.0001	0.83	0.83	9.19	0.0051		45.31	45.31	13.79	0.0009
X ₄	1	439.24	439.24	2660.7	< 0.0001		802.28	802.28	505.95	< 0.0001	421.72	421.72	4670.5	< 0.0001		644.89	644.89	196.36	< 0.0001
X ₅	1	29.84	29.84	180.77	< 0.0001		104.14	104.14	65.67	< 0.0001	26.47	26.47	293.17	< 0.0001		35.14	35.14	10.7	0.0028
X ₁ X ₂	1	22.03	22.03	133.44	< 0.0001		6.09	6.09	3.84	0.0597	21.65	21.65	239.75	< 0.0001		5.67	5.67	1.73	0.1992
X ₁ X ₃	1	48.29	48.29	292.52	< 0.0001		530.24	530.24	334.39	< 0.0001	44.37	44.37	491.37	< 0.0001		401.93	401.93	122.38	< 0.0001
X ₁ X ₄	1	15.14	15.14	91.7	< 0.0001		105.92	105.92	66.8	< 0.0001	19.03	19.03	210.8	< 0.0001		66.85	66.85	20.35	< 0.0001
X ₁ X ₅	1	0.034	0.034	0.21	0.6512		174.38	174.38	109.97	< 0.0001	0.22	0.22	2.49	0.1257		91.84	91.84	27.96	< 0.0001
X ₂ X ₃	1	35.76	35.76	216.65	< 0.0001		0.3	0.3	0.19	0.6666	32.4	32.4	358.84	< 0.0001		1.62	1.62	0.49	0.4887
X ₂ X ₄	1	9.56	9.56	57.91	< 0.0001		0.025	0.025	0.016	0.9003	12.7	12.7	140.66	< 0.0001		9.71	9.71	2.96	0.0961
X ₂ X ₅	1	6.15	6.15	37.26	< 0.0001		16.45	16.45	10.37	0.0031	4.8	4.8	53.21	< 0.0001		0.53	0.53	0.16	0.6914
X ₃ X ₄	1	34.72	34.72	210.29	< 0.0001		380.88	380.88	240.2	< 0.0001	33.05	33.05	366.01	< 0.0001		265.48	265.48	80.83	< 0.0001
X ₃ X ₅	1	20.72	20.72	125.52	< 0.0001		134.64	134.64	84.91	< 0.0001	20.35	20.35	225.4	< 0.0001		97.76	97.76	29.76	< 0.0001
X ₄ X ₅	1	9.71	9.71	58.84	< 0.0001		31.6	31.6	19.93	0.0001	10.63	10.63	117.68	< 0.0001		28.75	28.75	8.75	0.0061
X ₁ ²	1	0.61	0.61	3.71	0.0638		1.54	1.54	0.97	0.3323	0.68	0.68	7.5	0.0104		0.64	0.64	0.19	0.663
X ₂ ²	1	34.09	34.09	206.52	< 0.0001		59.12	59.12	37.28	< 0.0001	34.56	34.56	382.76	< 0.0001		21.79	21.79	6.63	0.0154
X ₃ ²	1	125.1	125.1	757.78	< 0.0001		3.96	3.96	2.5	0.1249	117.72	117.72	1303.7	< 0.0001		5.92	5.92	1.8	0.1898
X ₄ ²	1	26.3	26.3	159.31	< 0.0001		160.31	160.31	101.1	< 0.0001	25.89	25.89	286.74	< 0.0001		149.27	149.27	45.45	< 0.0001
X ₅ ²	1	72.87	72.87	441.43	< 0.0001		109.61	109.61	69.12	< 0.0001	69.93	69.93	774.43	< 0.0001		100.51	100.51	30.61	< 0.0001
Residual	29	4.79	0.17				45.98	1.59			2.62	0.09				95.24	3.28		
Lack of Fit	22	4.18	0.19	2.21	0.1423		27.67	1.26	0.48	0.9103	2.02	0.092	1.06	0.5033		76.93	3.5	1.34	0.365
Pure Error	7	0.6	0.086				18.31	2.62			0.6	0.086				18.31	2.62		
Cor Total	49	1032.97					3128.4				995.84					2367.24			

Table 3. Comparison of determination coefficient (R^2) for ANN and CCD models.

Analyte	CDD		ANN	
	MWCNT-PATMSPEDA	MWCNT-PATMSPEDA-Pd-NPs	MWCNT-PATMSPEDA	MWCNT-PATMSPEDA-Pd-NPs
SY	0.9853	0.9974	0.978	0.972
ER	0.9954	0.9598	0.971	0.971

Table4. Isotherm constant parameters calculated for the dyes adsorption onto adsorbents.

Isotherm	Equation	Parameters	MWCNT-PATMSPEDA				MWCNT-PATMSPEDA-Pd-NPs						
				ER		SY		ER		SY			
			0.02 g	0.03 g		0.02 g	0.03 g		0.02 g	0.03 g		0.02 g	0.03 g
Langmuir	Ce/qe = 1/(KaQm) + Ce/Qm	Qm (mg.g ⁻¹)	30/58	25/32		38/76	33/90		55/25	39/68		59/17	37/18
		Ka (L mg ⁻¹)	8/6	39/5		1/86	2/59		3/02	3/81		3/93	7/47
		R ²	0/9933	0/9941		0/9908	0/9754		0/996	0/995		0/998	0/992
Frendlich	Ln qe = ln KF + (1/n) ln Ce	1/n	0/2173	0/0611		0/1969	0/2294		0/63	0/98		0/66	0/56
		K _F (L mg ⁻¹)	20/41	22/65		24/68	23/01		5/59	5/03		6/33	5/50
		R ²	0/7988	0/5321		0/507	0/811		0/978	0/977		0/979	0/98
Temkin	qe = B ₁ ln KT + B ₁ lnCe	B ₁	4/7172	1/44		5/4213	5/7776		11/43	8/27		12/08	7/64
		K _T (L mg ⁻¹)	102/51	72/02		116/75	58/56		34/46	42/94		45/60	85/62
		R ²	0/7758	0/5064		0/4649	0/813		0/988	0/986		0/987	0/975
Dubinin-Radushkevich	Ln qe = ln Qm – Kε ²	Qs (mg g ⁻¹)	21/30	18/28		26/75	12/98		40/42	30/46		45/12	31/65
		B×10 ⁻⁷	-0/3	-0/2		-0/4	0-/6		-0/3	-0/3		-0/3	-0/2
		E	4098/36	5000		3533	10000		4081	4081		4081	5000
		R ²	0/944	0/934		38/76	33/90		0/783	/993		0/9715	0/987

Table 5. Comparison with some reported literatures.

Adsorbent	Dye	Contact time (min)	Adsorption capacity (mg/g)	References
Hen feathers	ER	90-120	1.754 mol/g	[43]
Activated carbon (AC)	ER	30	5.0×10^{-5} mol/L	[44]
Activated De-Oiled mustard (ADM)	ER	129	5.0×10^{-5} mol/L	[44]
Materials-Bottom Ash	ER	90	98.04%	[45]
Materials-Bottom De-Oiled Soya	ER	90	95.65%	[45]
MWCNT-PATMSPEDA	ER	3.88	30.58	our work
MWCNT-PATMSPEDA-Pd-NPs	ER	3.88	55.25	our work
ZnS: Ni-NP-AC	SY	3.8	-	[46]
CuS-NP-AC	SY	17	122	[47]
Zn(OH) ₂ -NP-AC	SY	30	158.7	[48]
Ionic liquid based PMO	SY	2.0	208	[49]
NiS-NP-AC	SY	15	333.3	[35]
SnO ₂ -NP-AC	SY	20	7.89	[50]
Wood activated carbon	SY	10	4.89	[51]
Orange activated carbon	SY	30	30.82	[51]
Zn(OH) ₂ -NP-AC	SY	5.2	83–114	[52]
MWCNT-PATMSPEDA	SY	3.88	38.76	our work
MWCNT-PATMSPEDA-Pd-NPs	SY	3.88	59.17	our work

Fig. 1. The steps for the synthesis of the adsorbent.

Fig. 2. Absorption spectra of SY and ER dyes in single and binary solutions (initial dye concentration for SY and ER was 8.0 mg L⁻¹).

Fig. 3. Topology of conventional P-S-P MLP.

Fig. 4. FT-IR spectra (a) and TG-DTG patterns (b) of the prepared samples.

Fig. 5. XRD patterns of the prepared samples.

Fig. 6. SEM images of the MWCNT (a) MWCNTs-PATMSPEDA (b) and MWCNTs-PATMSPEDA-Pd-NPs (c)

Fig. 7. The Actual values versus the predicted data of normalized simultaneous removal of dyes for MWCNTs-PATMSPEDA and MWCNTs-PATMSPEDA-Pd-NPs.

Fig. 8. Typical response surfaces and contour plot for interaction of variables in responses.

Fig. 9. Effect of the number of hidden layer neurons on AAD% of the ER and SY dyes removal by MWCNTs-PATMSPEDA (a) and MWCNTs-PATMSPEDA-Pd-NPs (b).

Fig. 10. Evolution of training, validation, and test errors as a function of the number of training epochs during ANN for the ER and SY dyes removal by MWCNTs-PATMSPEDA (a) and MWCNTs-PATMSPEDA-Pd-NPs (b).

Fig. 11. Modeling ability of the optimized ANN to predicate the ER (a) and (b) dyes removal by MWCNTs-PATMSPEDA and the ER (c) and SY (d) dyes removal by MWCNTs-PATMSPEDA-Pd-NPs

Fig. 12. AADs plot of the ER and SY dyes removal by MWCNTs-PATMSPEDA (a) MWCNTs-PATMSPEDA-Pd-NPs (b) from experimental data