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# 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-phenylallaylidene)-*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 constructing 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 ($R^2$) 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 $R^2$ 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.


## 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 consisting of beverage, jams, jelly, soup and sauces [4,5]. It should be avoided by anyone suffering from existing allergic (asthma or urticaria). It 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 is 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

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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 interesting to implement the most of these considerations and requirements [20,21]. Therefore, searching and designing of a novel adsorbent in this method is important. Multi-walled carbon nanotubes (MWCNTs) due to excellent mechanical, electrical and thermal properties have been 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 to 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-phenylallaylidene)-*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 aqueous 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 assistance 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 is 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].

## Experimental

### *Instruments and reagents*

Chemical reagents including *N*-(3-(trimethoxysilyl)-propyl) ethylenediamine, MWCNT, acetonitrile, cinnamaldehyde, SY, ER, $Na_2PdCl_4$, 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 equipments were used according to previous publication [32,36–41].

### *Preparation of MWCNT-PATMSPEDA-Pd-NPs*

At first step, trimethoxysilylpropylethylene diamine functionalized on MWCNT (MWCNT-$NH_2$) 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-phenylallaylidene)-*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 $Na_2PdCl_4$ 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.