Adsorption of Thymol Blue and Erythrosine-B on MWCNTs Functionalized by N-(3-nitrobenzylidene)-N'-'trimethoxysilylpropyl-ethane-1,2-diamine
Equilibrium, Kinetics and Thermodynamic Study

FARVEH RAOUFI, MAJID. MONAJJEMI and HOSSEIN AGHAIE*

1,2,3Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran.
*Corresponding author E-mail: Hn_Aghaie@yahoo.com

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ABSTRACT

We have accomplished a synthesized of an adsorption material through anchoring
N-(3nitro-benzeyliden)-N-trimethoxysilylpropylethan-1,2-diamin onto multi-wall-carbon nanotube.
The systems were established via SEM and FT-IR techniques. Then, it was used for removing the
ultra-sound-assisted for Thymol Blue (TB) and Erythrosine-B (EB). The pH dependency and initial
dyes concentration, sonication time and adsorbent's dosage for the removing percentage of
Thymol Blue and Erythrosine-B which have investigated by CCD or Central-Composite Designing.
It was exhibited that the Thymol Blue and Erythrosine-B adsorption follows, while the Langmuir
models explain the equilibriums variables.

Keywords: Multi-walled carbon nanotubes, Surface methodologies, Ultra sounded-assisted
dye removing, Thymol Blue (TB) and Erythrosine-B (EB)

INTRODUCTION

Dyes and pigments have been released
in the waste-waters from textiles, papers, rubbers,
plastics, leathers, cosmetics, foods, and drug
industries. These dyes make allergic dermatitis,
skins irritation, cancers and mutations in living
organism. It also causes eyes burn, which might be
reason for permanent injuries to the eye's human
and animal also. Discharge of a dye into waters
sources threaten the water supplies and qualities
due to irrefrangible under harshest condition,
toxicities, accumulations and magnifications
throughout the foods chain. The high colored's
effluents not only cause damages for living but
human being via producing mutagenic effects.

Dye generally has a complex aromatics
structure which makes them stables and difficulty
for decomposing. The dye presents in wastewater
absorbs sunlight's leading to decreasing in the
efficiencies of photo-synthesis in the aquatic plant
due to reducing lights penetration.

Among various types of dye including
anionic, cationic (basically dye), and non-anion
disperse dye), the positive ion is the most toxic
dyes. Among various methods of dye's removal
from aqueous solutions such as membrane separation are important. For the chemical oxide materials the adsorption techniques are known as an important methods for dye removal.

Thymol Blues, belongs to tri-phenyl-methane groups, have biological activities same stains agents. The TB dyes are also used for pH indicators in analytical chemistries. Inhalation leads to respiratory tract exposures and subsequently. Skin Contacts may causes irritations with redness and pain.

Erythrosine-B is a water-soluble xanthenes class of dye. It is extremely used as colorant in foods, textiles, drugs and cosmetics. In high dose it cause several types of allergies, thyroid activity, carcinogenities, DNA damages, and neurotoxicity's behavior in the human and animal. The photo-chemicals and bio-chemicals degradations of the erythrosine are not suggested because for formation toxic by-products. Adsorptions are the best techniques for removing of toxics and noxious impurity in comparison to other conventional protocols same as chemical coagulation, ion exchanges, electrolysis of electrolytes, biological treatment which are related to advantages. Adsorption technique also have a lot of efficiencies for the removing pollutant which are highly stables in biological degradations process through economically mild pathways. Of those methods nanomaterial's based adsorbent is highly recommended for dye pollutant removal. The suitable figures of merit in multi components dye system removing are based on development of novel methods which permits its accurate simultaneous determination of mixture. The encounters difficulty is serious peak overlapping that subsequently impossible for its direct determination in the mixtures using general equations like Beer–Lamberts. Derivatives spectroscopies efficiently are applicable for resolving absorption peak overlaps through its separations and corrections of background interference. These methods are based on searching the wavelength which able to accurate and repeatable monitoring for each specie in the complexes without no interferences from the other targets compounds. The classical optimization of protocols failed for giving useful information of interactions between several variables. Central composites design or CCD under surface methodologies can be applied for handling of both variable involving and response without suffers above-mentioned draw backs. These approaches enable us for making a suitable predicative models for applying several factor even in the presence of complexes interaction for describing and finding the best optimized condition with less times elapsed.

In this Paper, MWCNT has been modified with N-(3-nitro-benzylidene)- N-tri methoxy silylpropyl-ethane, 2diamine as the best adsorbents using FTIR and SEM. This adsorbent was used for the ultrasound-assisted removal of Thymol Blue and Erythrosine-B from aqueous solutions. The influences of variables initial Thymol Blue and Erythrosine-B as well as its interaction were investigated under response surface methodology.

**EXPERIMENTAL**

**Materials and instruments**

Thymol Blue and Erythrosine-B supply from Merck in Germany. The stocks solution of one hundred mg/l for every dyes were getting dissolutions of ten milligram of which in 100 milliliter double distilled waters, separately and are suitable dilute on performing for obtain worked solution with desired concentration. R, N-(3-(tri methoxysilyl)-propyl) ethylene diamine (TSPED) and 2-nitrobenzaldehyde (NBA) was purchased through SigmaAldrich. Multi-walled carbon nanotube was supplied via RiedelDeHean and other reagents was used for analytical grades in the Merck Company. The pH/Ion-meter was used for the pH measurement. Dye Thymol Blue and Erythrosine-B concentration was determined using Jasco UVVis spectrophotometric model V530, at wave-length of 430 nm and 580 nm, respectively. The ultrasonic bath including heating systems were used at frequencies 60Hz and power 130W. The morphologies of the NBATSPEDMWCNT were studied by SEM Hitachi, model S4160. The FTIR spectrophotometer for compound was recorded on the JASCO680 instrument in areaof 380-4200 cm⁻¹ using potassium bromide pellets with molratio.
Preparation of NBATSPED-MWCNT

At first step, tri methoxy silylpro pylene diamines support on MWCNT-(NH₂-MWCNT) were synthesized through the reactions of 1.85 ml N-(3-(tri methoxysilyl)-propyl) ethylene diamine and 0.15 gramm MWCNT in 20 milliliter of dichloromethan under reflux at forty degree in the oil bath for twenty four hours. Then, the obtained solids were filtered. The products were filtered, washed with fifty milliliters of C2H5OH, double distilled water and then dried in oven for 10 h 50 oC. These step are presented in the Fig.1.

Ultra-sounded-assist a-multicomponent adsorb of Thymol Blue (TB) and Erythrosine-B (EB) on to NBATSPED-MWCNT

The batches process using NBA..MWCNT in presence of ultrasounds were applied for binaries adsorption of Thymol Blue and Erythrosine-B. The vessels were immersed in the ultrasonic baths for four minutes at room temperature and then the solution was centrifuged.

Adsorption equilibrium study

The equation and parameter of the isotherm of the research has been reported in Tables 1 and 2, respectively. The desirabilities function create the function of every individual responses leading to the final outputs of the global functions (D), max values of which support the achievements for optimum value. The principles and applications of desirability functions for the best predications of real behaviors of adsorptions system were pointed out previously. The desirability's profile indicates the predicted level of variable, which produce the most desirable responses.

Table. 1: Equation model used in this study

<table>
<thead>
<tr>
<th>Linear equation</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>log.q = log K_F + log X</td>
<td>Freundlich isotherm</td>
</tr>
<tr>
<td>1 + q = (1 + (K_L q_m / X )q)</td>
<td>Langmuir isotherm</td>
</tr>
</tbody>
</table>

Table. 2: parameter applied in this work

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_F</td>
<td>Freundlich isotherm constant</td>
</tr>
<tr>
<td>n</td>
<td>Freundlich isotherm exponent</td>
</tr>
<tr>
<td>K_L</td>
<td>Langmuir constants</td>
</tr>
<tr>
<td>q_m</td>
<td>Maximum adsorption capacities</td>
</tr>
</tbody>
</table>

Table. 3: Confirmation of the adsorptions for a dye at specific homogeneous sites as the monolayers for NBATSPED-MWCNT surfaces
RESULTS AND DISCUSSION

Based on theoretical calculation for comparison to experimental data the references have been considered\textsuperscript{39-61}. And based the experiments results and approaches of related works this work has been investigated\textsuperscript{62-116}.

Characterization of adsorbents

The FT-IR spectrums of NBASPEDMWCN (Fig. 2b), exhibits absorption peaks at 1715 cm\(^{-1}\) correspond to the stretching modes of vibrations for carbonyl group. The broad peak at 1086 cm\(^{-1}\) could assign to carbon oxygen stretching from phenolic, alcoholic, etherics group. These peaks can be assigned to the OH groups of moistures and carboxylic groups\textsuperscript{34}. The aromatic\textsuperscript{16} C=C stretching are observed at 1459 cm\(^{-1}\). The FT-IR spectrums (Fig. 3b.) displays the new peaks as a weak shoulders at 2931 cm\(^{-1}\), which correspond to a stretching modes vibration for C–H bond in propyl\textsuperscript{35} groups.

Statistical analysis

Central composites are designed as the most applicable types of RSM were applies for modeling and optimizing of concentrations for TB (X\(_1\)) and EB (X\(_2\)), pH(X\(_3\)), amounts of adsorbent (X4) and (X5) on the ultrasonic-assisted\textsuperscript{36} adsorption of TB\textsuperscript{37} and EB\textsuperscript{38} dye through NBATSPED-MWCNT\textsuperscript{38}. 5 independent variable was set at five level at which the R\% of TB and EB dye as response were determined and exhibit in the Tables four and five. Analysis of the variance or ANOVA\textsuperscript{38} were performed for evaluating the important\textsuperscript{35} and effectives terms for modeling of the response based on F-test and p-values\textsuperscript{36-38}.

Analysis of central composite designing

ANOVA was performed for obtaining information of the most important variable and its possible interaction (Table 5). Generally, they applied for the model of 11.16 and 8.48 of TB and EB respectively. The value calculated of the determination coefficient are R\(^2\) 0.96 and 0.94 for TB and EB respectively. The removal percentage of for TB and EB has been calculated. Therefore, the following semi-empirical expression applies for models of the removal percentage (R\%) for TB and EB respectively\textsuperscript{36}.

For making other assessments on the applicability\textsuperscript{37} of the model, the predicted and observed value of the removal percentages of TB and EB dye on NBATSPED-MWCNT were compared in (Fig. 3).

R\%=95.709-2.1767X1-1.0258X2+0.94833X3+6.323X4+2.0955X5-14.350X1X2+1.3388X1X3+2.9638X1X4-1.1638X1X5+0.69000X2X3+1.0650X2X4-1.3900X2X5-1.6612X3X4+1.4612X3X5-1.9138X4X5+0.66726X1\(^2\)+0.91726X2\(^2\)-0.020244X3\(^2\)-2.8327X4\(^2\)-0.41595X5\(^2\) (5)

R\%=95.775-0.88250X1-1.3383X2+0.21167X3+6.323X4+2.0955X5-14.350X1X2+1.3388X1X3+2.9638X1X4-1.1638X1X5+0.69000X2X3+1.0650X2X4-1.3900X2X5-1.6612X3X4+1.4612X3X5-1.9138X4X5+0.66726X1\(^2\)+0.91726X2\(^2\)-0.020244X3\(^2\)-2.8327X4\(^2\)-0.41595X5\(^2\) (6)

Response surface methodologies

Fig (3a, b) exhibits the removal percentages change versus the adsorbents dosages. The positive increasing in the dyes removal percentages with
Table 6: Several isotherms including the correlation coefficient calculation dyes adsorption over NBATSPED-MWCNT

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Equation</th>
<th>Parameters</th>
<th>Value of Parameters for TB (0.025g)</th>
<th>Value of Parameters for EB (0.025g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_e = \frac{q_m b C_e}{1 + b C_e}$</td>
<td>$Q_m$ (mg g$^{-1}$)</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_a$ (L mg$^{-1}$)</td>
<td>1.53</td>
<td>0.487</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.997</td>
<td>0.998</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$</td>
<td>$1/n$</td>
<td>0.24</td>
<td>0.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$K_F$ (L mg$^{-1}$)</td>
<td>3.66</td>
<td>4.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>0.985</td>
<td>0.982</td>
</tr>
</tbody>
</table>

Increasing in the adsorbent masses can be seen. Significant diminishment in removal percentages at lower amounts of NBATSPED-MWCN are attributed to higher ratio of dyes molecules. Fig. (3c) exhibits sonication times can be concluded the maximum adsorption of EB could be riches when the sonication times were increased. Fig (3d) exhibits the removal percentages changing versus the adsorbent dosages.

**Fig. 3.** Surface of several dyes removing: (a) pH- adsorb dosages, (b) Time- adsorb dosages, (c) Time-concentrations of TB, Dosage-concentrations EB
CONCLUSION

Sonication's methods are effective, very fast and sensitive to adsorbed materials compared to other methods especially for the removal of Thymol Blue and Erythrosine-B. The influence of experiment parameters such as various pH, sonication times, NBATPED-MWCNT dosages, initial TB concentrations and initial EB concentrations. The removal of TB and EB forms aqueous solution in short
time 5 min. are feasible with high removal percentages at optimum pH (6.5) which are neutral and are advantages for the adsorption process.

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