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Research Article

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Quantitative Structure Activity Relationship (QSAR) Modeling for Studying the Stability of Organic Dyes by Tio_2 Photocatalyst

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ABSTRACT

Background: Chemical and organic dyes used in different industries are responsible for some environmental hazards. Photocatalytic degradation in certain wavelength is a promising technique to overcome this problem. However, identifying and choosing a suitable photocatalyst is a cumbersome process.
Methods: Modeling as well as structure and molecular properties have been used as a tool for identifying photocatalysts. For photocatalyst degradation experiment, different concentration of organic dye analyzed with TiO_2 in different time and temperature. Absorption of the solution shows the degradation of dye.
Results: In the present study, quantitative structure activity relationship (QSAR) modeling of dye degradation by TiO_2 photocatalyst has been performed for efficient elimination of hazardous effects of the commercial dyes. Here, the 3D structure and stable mode of the dye molecules, such as methylene blue, methyl red, acid fuchsin, and methyl orange were analyzed using quantum mechanics methods. The quantitative structure activity relationship computations were performed assuming that the cyclic structure of the compounds is considerably proportionate with their color and wavelength, as well as their stability energy.
Conclusions: The results indicate successful photocatalytic degradation of the chemical dyes using TiO_2.

Keywords: Synthetic dye; QSAR; Photocatalyst; Titanium dioxide

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INTRODUCTION

The synthetic dyes that are used in different industrial processes are associated with certain environmental hazards along with emerging health risks when consumed in larger scale [1]. The conventional ways of treatment may further release more toxic substances, and generate large volume of solid wastes. Hence, photocatalysis has proved to be an alternative technique that has been successfully employed for degradation of the synthetic dyes as well as environmental remediation. The characteristics of Titanium dioxide (TiO_2), such as low toxicity, high reactivity, chemical stability and cost-effectiveness have led to its wider applicability in the field of photocatalysis.

In order to understand and accelerate the process of dye degradation, knowledge about the molecular structure of the dye molecules is necessary [2]. The quantitative structure activity relationship (QSAR) will help us understand the correlation between the chemical structure and associated biological activity [3].

Hence, the present study aimed at studying the degradation process of the synthetic or chemical dye molecules by the photocatalytic TiO_2 through QSAR modeling.

EXPERIMENTAL SECTION

At first the pigments' structure were drawn via Gauss View software, and subsequently optimized through Guassian03 software and B3LYP/6-31G method. Next, to conduct QSAR computations, the optimized structure was entered into DRAGON software and conformers' computations were performed.

RESULTS AND DISCUSSION

For computing some of the conformers (compounds with a particular molecular structure), we need to get familiar with the 3D structure and stable mode of the molecules. Thus, the molecular structure needs to be optimized using quantum mechanics methods. For this purpose, at first the pigments' structure were drawn via Gauss View software, and subsequently optimized through Guassian03 software and B3LYP/6-31G method. Next, to conduct QSAR computations, the optimized structure was entered into DRAGON software and conformers' computations were performed. The selected molecules were pigments with several different applications. In addition, these structures are classified as unsaturated cyclic compounds with hetero-atom. All of these molecules are referred to as hazardous compounds. We assumed that the cyclic structure of these compounds was considerably proportionate with their color type and wavelength as well as stability energy. Moreover, in the presence of photo catalytic materials, the percentage of damage caused to these compounds can be determined as the function of stability energy (optimized energy of structure). Figure 1 presents the computed photocatalyst properties in relation to the values of experimental photocatalyst properties for molecules of the predicting series. So, we performed this procedure only for evaluation of the linear model.

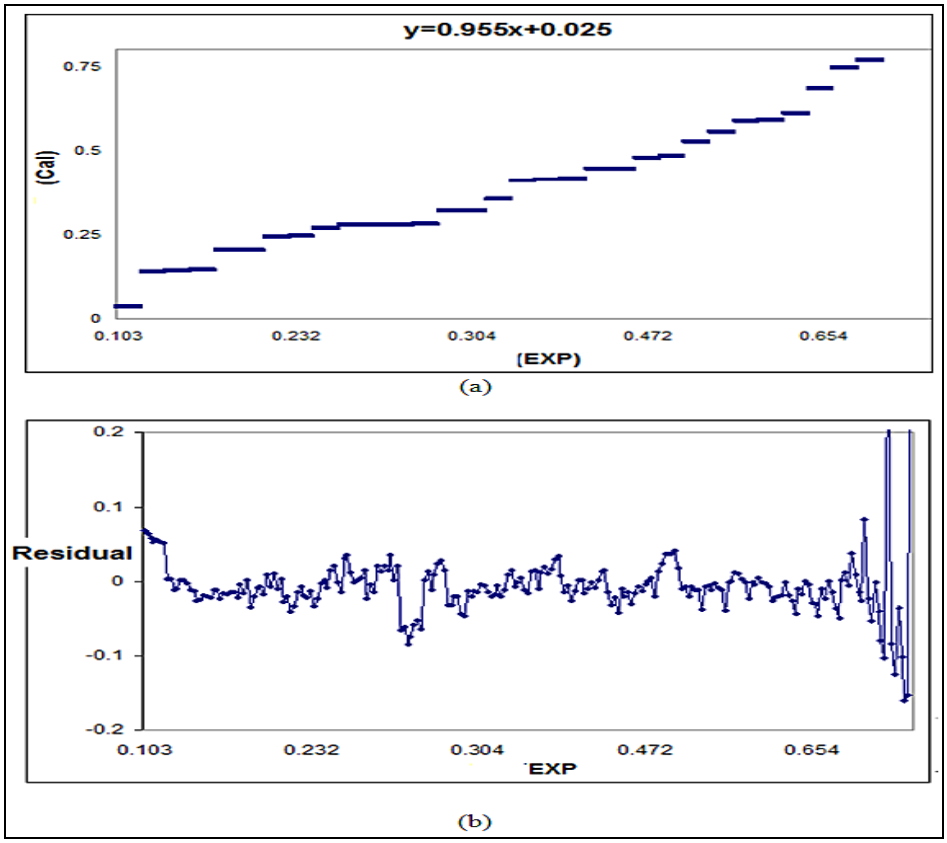

Figure 1: Values of selected model evaluation for percentage of pigment damage.
(a) Photocatalytic properties computed y model in relation to experimental photocatalytic properties.
(b) Residual values in relation to experimental photocatalytic properties values.

In order to conduct modeling and gaining the best possible model, we used multiple linear regression (MLR) and step technique. A number of strategies were applied. Firstly, the entire conformers were categorized into four groups: topological, electronic, geometrical and physicochemical. Then, regression technique was performed for each single block through different Howard orders and step method [1]. During these stages, several different models were obtained. Further, to increase the chance of using more conformers in the model, we employed conformers' elimination method. In this technique, one of the entered variables was removed from the model, and was followed by regression. Again, the same variable was entered leading to the removal of another variable with subsequent regression. Accordingly, we could obtain greater models with more diverse conformers. In fact, an appropriate model is selected on the basis of highest number of R and F, and the lowest number of conformers and standard deviation. Table 1 illustrates statistical features of these models for the reference series. As it is seen, among these models, models 3, 5, 9 and 12 have the highest F and R and the lowest number of conformers and standard deviation. So, they are considered as appropriate models.

Table 1: Modeled patterns by multiple linear regression (MLR) technique

Model	R (regression coefficient)	Adj-R^2 (Adjusted R^2)	Std. Error	F (F-Factor)	N (number of occupy)
1	0.948	0.897	0.082	1135	5
2	0.947	0.897	0.083	1893	5
3*	0.959	0.920	0.073	2489	3
4	0.939	0.882	0.088	1614	6
5*	0.957	0.916	0.074	2352	3
6	0.921	0.848	0.099	1460	6
7	0.901	0.810	0.110	1306	5
8	0.953	0.907	0.078	1587	4
9*	0.958	0.918	0.073	2431	3
10	0.889	0.790	0.138	983	6
11	0.956	0.913	0.076	1358	6
12*	0.958	0.918	0.073	2427	3
13	0.905	0.819	0.102	1204	4
14	0.959	0.918	0.073	1829	6
15	0.943	0.888	0.086	1718	5
16	0.945	0.892	0.084	1794	5
17	0.947	0.897	0.082	1893	4
18	0.939	0.882	0.088	1614	3
19	0.899	0.808	0.125	1105	6
20	0.893	0.797	0.131	995	5

Unlike previous works on modeling [4-7], in the present study we attempted to consider the overall behavior of molecules in relation to its photocatalytic properties. Modeling of identical conformers that demonstrated different aspects of interactions with photocatalyst were provided. Subsequently, the conformers were selected as the independent variables. The photocatalyst properties were selected as the dependent variable in form of a mathematical equation.

Y (%TiO_2 Degradation= 0.04A+0.89B+0.0059C+…)
A, B and C are the important factor effected to degradation of photocatalyst. Subsequent to the specification of independent and dependent variables using SPSS software and multiple linear regression method, firstly, we opted for a series of good conformers out of the entire conformers. Secondly, we created certain linear equations between the conformers and photocatalyst properties as the QSAR modeling percentage of degradation is a dependent parameter and all parameters that Dragon software has analyzed are independent. For computation of some conformers, it was required to have 3D structure and stable mode of molecules. Prior to the computations, the molecule structures were optimized on the basis of quantum mechanics methods [8]. In this study postulated that chemical interaction caused the degradation but by QSAR showed structural and molecular parameters also affected the degradation.

Moreover, as the most stable conformers were used in its gaseous form for each category, we computed enthalpy of formation (heat of formation) for different conformers of each compound. Next, according to the numerical value of enthalpy of formation of structure, the most negative enthalpy of formation referred to the best conformer. For all molecules of the data series, the stable conformer was similarly computed. Following molecules optimization, we applied DRAGON software to compute conformers. To the end, we entered data relevant to the existing compounds in reference series and predicting series into the DRAGON software separately, and 1497 conformers were computed for each category. Based on this computations, we excluded those conformers without any statistical significance value, i.e., zero or constant values or r>0.95.

Of the total conformers, 418 with constant or zero values, and 783 conformers with r>0.95 were removed.
The MLR and step techniques were used for the modeling process generated 24 (4!) models. Further, to increase the chance of using more conformers in the model, conformer elimination method was employed by which diverse conformers were obtained.

CONCLUSION

Specification of independent and dependent variables using multiple linear regression method, firstly, we opted for a series of good conformers out of the entire conformers. Secondly, the created certain linear equations between the conformers and photocatalyst properties. For QSAR modeling percentage of degradation is dependent parameter and all parameters that Dragon software has analyzed are independent. For computation of some conformers, it was required to have 3D structure and stable mode of molecules. Prior to the computations, the molecule structures were optimized on the basis of quantum mechanics methods. In this study postulated that chemical interaction caused the degradation but by QSAR showed structural and molecular parameters also

affected the degradation [9]. The MLR and Step techniques used for the modeling process generated 24 (4!) models. Further, to increase the chance of using more conformers in the model, conformer elimination method was employed by which diverse conformers were obtained.

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