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An ESR Study on 2,4 Diaminotoluene Exposed to Gamma Rays and Application of Machine Learning

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The polycrystals of 2,4 diaminotoluene were produced by slow evaporation of solvent. The polycrystalline samples were exposed to ^{60}Co gamma rays with dose rate of 0.950 kGy/h, at room temperature, for 12, 24, 48, and 72 hours. The electron paramagnetic resonance measurements were carried out on these samples in the temperature range between 298 K and 400 K. No electron paramagnetic resonance signal was observed in the samples irradiated for 12, 24, 48 hours. Two types of radicals were detected using ESR spectrometer in the sample irradiated for 72 h. These radiation damage centers were called RI and RII. The average values of g and the hyperfine coupling constant were calculated. This study also investigates the potential usage of machine learning methods and aims to test the success of these methods and to select the best method.

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1. Introduction

Aromatic amine groups are used as industrial chemicals and they are environmental pollutants. 2,4 diaminotoluene appertain to amine group. This chemical material is a synthetic intermediate [1] and it is used in the plastics industries and in the production of dyes nowadays [2]. 2,4-diaminotoluene has exhibited toxic properties in liver tissues [3]. Due to toxic properties of the aromatic amine groups, investigations of biological activities of the amine groups have been extensive. International Agency of Research on Cancer (IARC) has concluded that this compound is likely to be a human carcinogen. However, no information about the mechanism underlying the toxicity of amine groups is available.

In our study, we have focused on the fact that irradiation has a significant impact on the materials [4]. Ionizing radiation is able to kill the pathogens in contaminated foods. However, irradiation can results in breaking of bonds and changing of structural properties of the samples [5–7]. We have used electron paramagnetic resonance (EPR) method to study the radical formation mechanisms in 2,4 diaminotoluene exposed to radiation. The EPR technique has been frequently used for identification of radiation damage centers in organic and inorganic substances [8–10]. In this study we also present the comparison of different machine learning methods to test the performance and to select the best method, which could be implemented theoretically. In our previous paper [11] we used a large data set. In the present case the number of data was limited to three data sets and we wanted to test the performance of machine learning methods in this case. Unlike in our previous work, the results of training and tests were compared separately for two data sets and in this way the best method has been selected.

2. Material and methods

2.1. Experimental

2,4 diaminotoluene was purchased from Sigma-Aldrich. Polycrystal formulations for each test chemical were produced in laboratory. The samples were irradiated for 12, 24, 48 and 72 h using ^{60}Co γ-ray source with dose rate of 0.950 kGy/h. The measurements of EPR were made using Bruker EMX 081 EPR spectrometer. The temperature measurements were carried out between 298 K and 400 K using a Bruker temperature control unit. During EPR measurements the modulation frequency was 100 kHz and the modulation amplitude was 2 G.

2.2. Theoretical

2.2.1. Machine learning method

Machine learning is the common name of the computer algorithms that model a given problem according to the data from the environment of the problem. Machine learning is a method of data analysis which includes automatic computing procedures based on logical or binary operations [12]. Artificial neural networks, decision trees, bayesian networks, support vector machines are examples of machine learning methods. In the application of machine learning methods, available data are divided into two sets. The first set of data is used for the "training"

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(learning) phase, and then the success of the learning is "tested" using second data set.

3. Results and discussion

EPR signals were measured on the sample irradiated for 72 hours. Following the irradiation of 2,4 diaminotoluene, the EPR measurements were performed between 298 K and 400 K. It was observed that the spectra depend slightly on the temperature. As the signal observed at 298 K consisted of four lines, the signal observed at 340 K consisted of six lines. Temperature affects localized or unlocalized state of an unpaired electron. Once the general condition of the spectrum was observed, it was seen that there was no essential change in the spectrum.

The temperature dependence of the EPR lines is shown in Fig. 1.

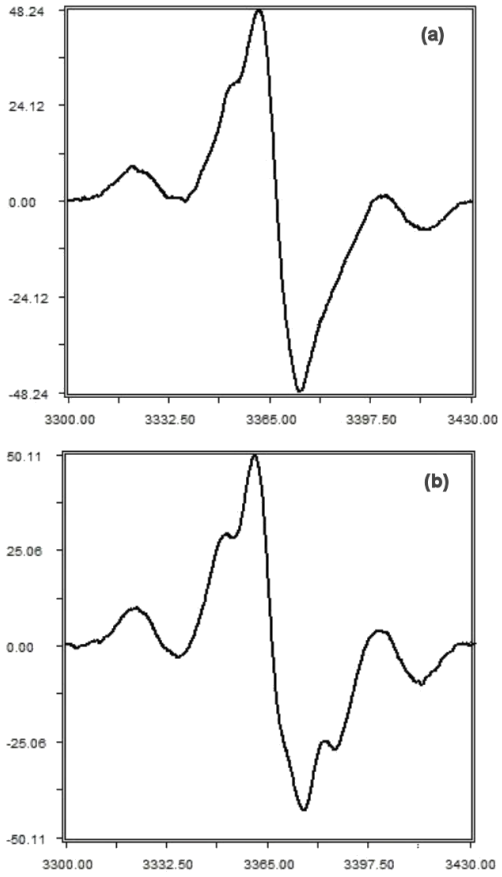

Fig. 1. The EPR spectrum of γ-irradiated 2,4 diaminotoluene at (a) 298 K and (b) 340 K.

When the recorded spectra were analysed, it was found that EPR lines belong to two radicals. According to the molecular structure of the sample and the recorded spectra, for the first radical, the contributions to the spectra came from H_a and H_b protons, magnetically equivalent; and then from the N_c proton. Similarly, for the second radical, contributions to the spectra came from H_x atom and from N_y proton (Fig. 2). These results were verified by computer simulation results shown in Fig. 3. The principle values and the g-tensors are given in Table I.

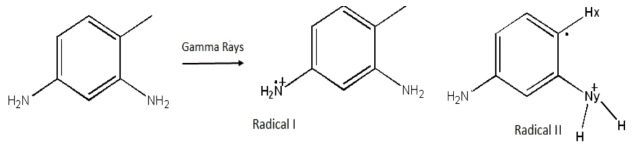

Fig. 2. Molecular structure of radical I (a) and radical II (b).

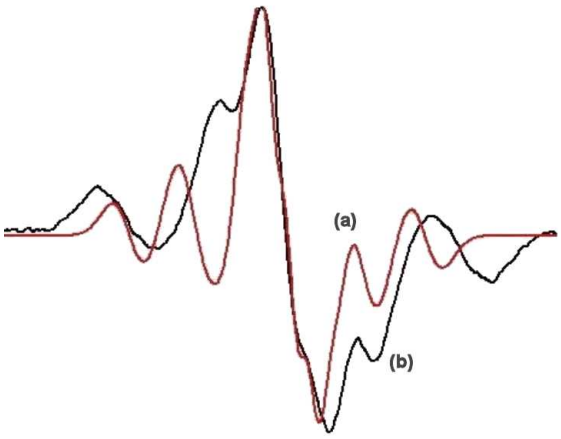

Fig. 3. The EPR spectrum (a) and its simulation (b).

TABLE I

The EPR parameters of irradiated 2,4 diaminotoluene.

	Radical I	Radical II
Hyperfine constant	$N = 20$ G $2H = 14.65$ G	$N = 2.87$ G $H = 7.15$ G
g-value	2.0077	2.0011

At this theoretical implementation phase, in total three data sets were used in this study and two of them (320 K and 400 K) were chosen to determine the methods. In the application of machine learning methods, firstly two data sets, not including their values, were used for training for ten-fold cross validation in the Weka Explorer, to determine the methods having the smallest error values. Seven methods having error rate less than 30% were listed and statistical results are shown for each training set in Table II.

Success of the top five (error rate less than 15%) learning methods was tested separately for 320 K and 400 K. Statistical values of the test phase are listed in Table III for each test set.

TABLE II

Statistical values of the training phase.

Method	T [K]	Correlation coefficient	Mean absolute error	Root mean squared error	Relative absolute error [%]	Root relative squared error[%]
Lazy IBk	320	0.9998	4.346	7.259	1.729	1.920
	400	0.9998	4.477	7.407	1.720	1.920
Bagging REPTree	320	0.9993	9.281	13.684	3.692	3.620
	400	0.9990	10.745	17.473	4.120	4.530
REPTree	320	0.9988	12.280	18.712	4.885	4.950
	400	0.9984	14.309	21.830	5.482	5.660
M5P	320	0.9952	25.275	40.607	10.054	10.742
	400	0.9955	26.804	41.029	10.269	10.638
M5Rules	320	0.9942	28.589	41.453	11.372	10.966
	400	0.9915	35.753	53.161	13.698	13.783
Regression by discretization	320	0.9884	49.898	57.455	19.849	15.199
	400	0.9885	50.070	58.289	19.180	15.110
MLP regressor	320	0.9839	55.702	67.616	22.157	17.887
	400	0.9750	69.895	85.635	26.780	22.200

TABLE III

Statistical values of the test phase.

Method	T [K]	Correlation coefficient	Mean absolute error	Root mean squared error	Relative absolute error [%]	Root relative squared error [%]
Lazy IBk	320	0.9848	46.708	67.409	17.662	17.598
	400	0.9914	33.712	51.670	13.749	14.062
Bagging REPTree	320	0.9857	44.964	64.874	17.003	16.936
	400	0.9925	31.615	48.823	12.894	13.287
REPTree	320	0.9850	46.426	66.677	17.556	17.407
	400	0.9914	33.401	51.557	13.622	14.031
M5P	320	0.9846	48.721	67.711	18.424	17.677
	400	0.9437	74.516	123.991	30.390	33.743
M5Rules	320	0.9846	50.791	70.618	19.206	18.436
	400	0.8968	98.510	170.260	40.176	46.335

While Lazy IBK method was having the best results in the training phase, Bagging REPTree method had better results than Lazy IBK by a narrow margin. Comparison of actual values and predicted values obtained by Lazy IBK and by Bagging REPTree are shown in Figs. 4 and 5 respectively, for test phase.

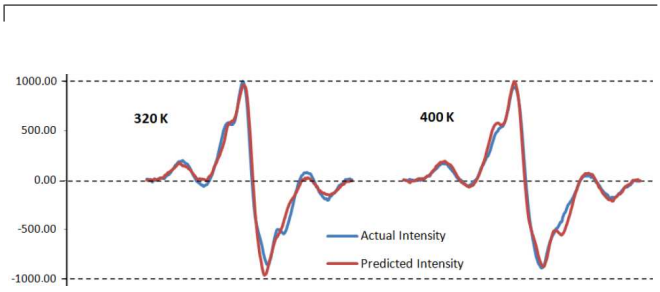

Fig. 4. Comparison of actual and predicted values for test phase (Lazy IBK method).

4. Conclusions

We have investigated the EPR spectral parameters of irradiated 2,4 diaminotoluene. This investigation has pointed out that the unirradiated substance and substance irradiated for 12, 24 and 48 hours do not give any EPR signal, however two types of radicals were produced in the sample irradiated for 72 h. It was observed that the spectra depend slightly on temperature. Theoretical results obtained using machine learning methods have shown that the machine learning methods can be used successfully for subsequent studies with large and small data sets. While Lazy IBK method was having the best results in training phase, Bagging REPTree method had better results than Lazy IBK in the test phase. The difference between the results obtained in the test phase of Lazy IBK and Bagging RepTree are very low, so we can state that both of them can be used successfully.

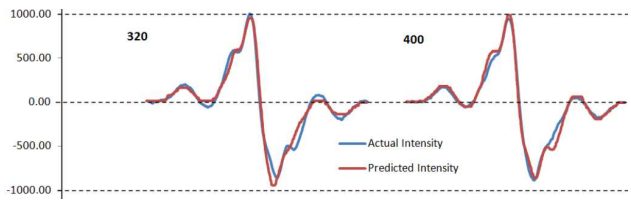

Fig. 5. Comparison of actual and predicted values for test phase (Bagging REPTree method).

Acknowledgments

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