ON RANDIĆ INDICES OF SINGLE-WALLED TiO$_2$ NANOTUBES

Wei GAO$^1$, Shakila BABY$^2$, Muhammad Kashif SHAFIQ$^3$
Hafiz Muhammad Afzal SIDDIQUI$^4$, Mohammad R. FARAHANI$^5$

In mathematical chemistry several topological indices have been introduced that can be classified as: (i). distance-based topological indices and (ii). degree-based topological indices. Each index measures some specific property of the molecular structure. In QSAR study, physico-chemical properties and topological indices such as Zagreb, Randić, ABC indices are used to predict the bioactivity of chemical compounds. Graph theory plays a vital role in this area of research. In this paper we present the formulas of general Randić, reduced Randić and reduced reciprocal Randić indices for two types of single-walled titania nanotubes (SW TiO$_2$ NTs) based on their structural layers in underlying chemical structure: 3-layered SW TiO$_2$ NTs and 6-layered SW TiO$_2$ NTs.

Keywords: TiO$_2$ nanotubes, Topological indices, Randić index, Reduced Randić index, Reduced reciprocal Randić index

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1. Introduction

The branch of chemistry in which we discuss and predict the molecular properties by using mathematical tools without referring to quantum mechanics is called mathematical chemistry [1,2]. The branch of mathematical chemistry which applies graph theory to mathematical modeling of chemical phenomena is known as chemical graph theory [2]. This theory is much beneficial in the development of the chemical sciences.

A molecular graph is a simple graph in which we show atoms by vertices

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$^1$ School of Information Science and Technology, Yunnan Normal University, Kunming China, e-mail: gaowei@ynnu.edu.cn

$^2$ Department of Mathematics, Government College University Faisalabad (GCUF), Pakistan, e-mail: shakilashahid2015@gmail.com

$^3$ Department of Mathematics, Government College University Faisalabad (GCUF), Pakistan, e-mail: kashif4v@gmail.com

$^4$ Department of Mathematics, COMSATS Institute of Information Technology (CIIT), Lahore, Pakistan.

$^5$ Department of Applied Mathematics of Iran University of Science and Technology (IUST), Narmak, Tehran, Iran, e-mail: MrFarahani88@gmail.com
and chemical bonds between these atoms by edges, where the hydrogen atoms are often omitted. Let G be a molecular graph with vertex set \(V(G)\) and edge set \(E(G)\). The cardinalities of the sets \(V(G)\) and \(E(G)\) are called order and size of G, respectively. An edge in \(E(G)\) with end vertices \(u\) and \(v\) is denoted by \(uv\). The vertices having an edge between them are called adjacent vertices. The set of all vertices adjacent to the vertex \(u\) is called the neighborhood of \(u\) and is denoted by \(N(u)\). The degree of \(u\) in \(G\) is defined as the cardinality of \(N(u)\) and is denoted by \(d_u(G)\).

These indices describe the structure and the branching pattern of the molecule numerically. So, the topological analysis of a molecule assigns unique number (index) to the structure of the molecule. This unique number may be considered as descriptor of the molecule under observation. The topological indices play a significant role in quantitative structure-activity research (QSAR) and structure-property relationships research (QSPR) study. In the QSAR study, topological indices such as Zagreb index, Wiener index, Szeged index, Randić index and ABC index are used to predict bioactivity of the chemical compounds.

Titania (TiO\(_2\)) is one of the most comprehensively studied metal oxide substances due to its wide spread applications in production of catalytic, gas-sensing and corrosion-resistance materials [3]. TiO\(_2\) attracts considerable technological interest due to unique properties in biology, optics, electronics and photo-chemistry [4]. Recent experimental studies show that titania nanotubes (TiO\(_2\) NTs) improve TiO\(_2\) bulk properties for photocatalysis, hydrogen-sensing and photo-voltaic applications [5]. TiO\(_2\) NTs have been fabricated by a number of different methods, such as hydrothermal treatment, template-assistant deposition and others. Various TiO\(_2\) NTs were observed in two types of morphologies: multi-walled (MW) cylindrical and scroll-like frequently containing various types of defects and impurities [6].

Although the first vertex-degree-based structure descriptors were the graph invariants that are known as first and second Zagreb indices [7, 8]. But these were used for a different purpose and were included among topological indices in 1983 by Balaban et al. [9]. However, the first genuine degree-based topological index was put forward in 1975 by Milan Randić [10]. His index was defined as

\[
R = R(G) = \sum_{uv \in E(G)} \frac{1}{\sqrt{d_u(G)d_v(G)}}
\]

Randić himself named it, “branching index” but soon it was re-named, “connectivity index” [11, 12]. Now it is reffered as, “Randić index”. It is the fact that Randić index is the most studied, most often applied and most popular among all topological indices. The number of papers devoted to this graph invariant is in hundreds. A few books are also written on this structure descriptor. The suitability of the Randić index for drug design was recognized [8, 10] and the index was used for this purpose. The general Randić index was proposed by Bollobás [13]
and Amic et al. [14] independently, in 1998 and was defined as

$$ R_\alpha (G) = \sum_{\{u,v\} \in E(G)} (d_u (G)d_v (G))^\alpha, $$

where $\alpha$ is a variable parameter.

The reciprocal Randić index is defined as

$$ RR = RR(G) = \sum_{\{u,v\} \in E(G)} \frac{1}{d_u (G)d_v (G)} $$

It is of course a special case of the much examined, “general Randić index” $ R_\alpha (G) = \sum_{\{u,v\} \in E(G)} (d_u (G)d_v (G))^\alpha, $ where $\alpha$ is a variable parameter [15, 16].

The reduced reciprocal Randić index, that is the reduced analogue of the reciprocal Randić index and is defined as

$$ RRR = RRR(G) = \sum_{\{u,v\} \in E(G)} \sqrt{(d_u (G) - 1)(d_v (G) - 1)} $$

In this paper we study two types of TiO$_2$ NTs based on their structural layers in underlying chemical structure: 3-Layered SW TiO$_2$ NTs and 6-Layered SW TiO$_2$ NTs. We will compute all of the above mentioned degree-based topological indices for these structures.

2. Randić indices for 3-layered SW TiO$_2$ NTs

The existence of TiO$_2$ NTs, in nature is in two forms namely, single-walled titania nanotubes (SW TiO$_2$ NTs) and multi-walled titania nanotubes (MW TiO$_2$ NTs). We are considering their chemical graphs because our aim is to work on molecular descriptors. For this reason our choice is ultimately, SW TiO$_2$ NTs. The three mineral forms of titanium dioxide are anatase, brookite and rutile [17]. The energetically stable anatase surface contains either six (O–Ti–O–O–Ti–O) or three (O–Ti–O) layers [17]. The two-periodic (2D) sheets cut from this anatase surface are used to form the TiO$_2$ NTs. If $p$ and $q$ are number of titanium atoms in each column and row respectively then the 2-parametric chemical graph of 3-layered SW TiO$_2$ NTs is denoted as TNT$_3$ [p,q], which can be viewed in Fig. 2.1.
The size of TNT₃ [p,q] is 12pq+2q. There are four kinds of edges corresponding to their degrees of end vertices which are:

\[ E_{2,4} = \{ uv \in E(G) \mid d_u(G) = 2 \text{ and } d_v(G) = 4 \} \]
\[ E_{3,4} = \{ uv \in E(G) \mid d_u(G) = 3 \text{ and } d_v(G) = 4 \} \]
\[ E_{2,6} = \{ uv \in E(G) \mid d_u(G) = 2 \text{ and } d_v(G) = 6 \} \]
\[ E_{3,6} = \{ uv \in E(G) \mid d_u(G) = 3 \text{ and } d_v(G) = 6 \} \]

The edge partition of edge set of the 3-layered SW TiO₂ NTs along with their cardinalities is shown in Table 2.1.

<table>
<thead>
<tr>
<th>Edge partition of edge set of TNT₃ [p,q]</th>
<th>E₁</th>
<th>E₂</th>
<th>E₃,4</th>
<th>E₃,6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardinality of ( E_{d_u, d_v} )</td>
<td>4p</td>
<td>4p</td>
<td>4p</td>
<td>2p(6q-5)</td>
</tr>
</tbody>
</table>

Now we present the formulae of Randić indices for 3-layered SW TiO₂ NTs by use the edge partitions given in Table 2.1.

**Theorem 2.1.** The general Randić index for 3-layered SW TiO₂ NTs is given by

\[ R_\alpha (G) = [2^{\alpha+1} p (2^\alpha + 2.3^\alpha) + 3^{2\alpha} (6q - 5)] 2^{\alpha+1} p \]

**Proof.** Since \( R_\alpha (G) = \sum_{uv \in E(G)} (d_u(G) d_v(G))^\alpha \)

\[ = 8^\alpha \mid E_{2,4} \mid + (12)^\alpha \mid E_{3,4} \mid + (12)^\alpha \mid E_{2,6} \mid + (18)^\alpha \mid E_{3,6} \mid \]

\[ = 4p8^\alpha + 4p(12)^\alpha + 4p(12)^\alpha + 2p(6q-5)(18)^\alpha \]

\[ = [2^{\alpha+1} (2^\alpha + 2.3^\alpha) + 3^{2\alpha} (6q - 5)] 2^{\alpha+1} p \]

**Theorem 2.2.** The Randić indices for 3-layered SW TiO₂ NTs for \( \alpha = -1, 1, -1 \) are as under

(i). \( R\frac{1}{2} (G) = RR(G) = [8\sqrt{3} + \sqrt{2}(18q - 11)] 2p \)

(ii). \( R\frac{1}{2} (G) = \frac{2\sqrt{2}}{3} (3q - 1 + \sqrt{6}) p \)

(iii). \( R\frac{1}{2} (G) = 4p(54q - 13) \)

(iv). \( R\frac{1}{2} (G) = \frac{p}{18} (12q + 11) \)

**Proof.** (i). \( R\frac{1}{2} (G) = RR(G) = \sum_{uv \in E(G)} \sqrt{d_u(G) d_v(G)} \)

\[ = \sqrt{8} \mid E_{2,4} \mid + \sqrt{12} \mid E_{3,4} \mid + \sqrt{12} \mid E_{2,6} \mid + \sqrt{18} \mid E_{3,6} \mid \]
= 4p\sqrt{8} + 4p\sqrt{12} + 4p\sqrt{12} + 2p(6q-5)\sqrt{18} = [8\sqrt{3} + \sqrt{2}(18q-11)]2p

(ii). \( R^{-\frac{1}{2}}(G) = \frac{1}{\sqrt{d_x(G)d_y(G)}} \)

= \frac{1}{\sqrt{8}} |E_{2,4}| + \frac{1}{\sqrt{12}} |E_{3,4}| + \frac{1}{\sqrt{12}} |E_{2,6}| + \frac{1}{\sqrt{18}} |E_{3,6}|

= \frac{4p}{\sqrt{8}} + \frac{4p}{\sqrt{12}} + \frac{4p}{\sqrt{12}} + \frac{12pq-10p}{\sqrt{18}} = \frac{2\sqrt{2}p}{3}(3q-1+\sqrt{6})

(iii). \( R(G) = \sum_{\text{ave}E(G)} d_x(G)d_y(G) \)

= 8 |E_{2,4}| + 12 |E_{3,4}| + 12 |E_{2,6}| + 18 |E_{3,6}|

= 4p(8) + 4p(12) + 4p(12) + (12pq-10p)(18) = 4p(54q-13)

(iv). \( R_{-1}(G) = \sum_{\text{ave}E(G)} \frac{1}{d_x(G)d_y(G)} \)

= \frac{1}{8} |E_{2,4}| + \frac{1}{12} |E_{3,4}| + \frac{1}{12} |E_{2,6}| + \frac{1}{18} |E_{3,6}|

= \frac{4p}{8} + \frac{4p}{12} + \frac{4p}{12} + \frac{12pq-10p}{18} = \frac{p}{18}(12q+11)

For the choice of \( \alpha = \frac{1}{2} \), the general Randić index becomes reduced Randić index and for \( \alpha = 1 \) it reduces to second Zagreb index. Because of this we have tested the general Randić index for \( \alpha = \frac{1}{2}, \frac{1}{2}, 1, -1 \).

**Theorem 2.3.** The reduced reciprocal Randić index for 3-layered SW TiO\textsubscript{2} NTs is given by

\[ RRR(G) = 4p(\sqrt{3} + \sqrt{5} + \sqrt{6}) + 2\sqrt{10}p(6q-5) \]

**Proof.** \( RRR(G) = \sum_{\text{ave}E(G)} (d_x(G)-1)(d_y(G)-1) \)

= \( \sqrt{3} |E_{2,4}| + \sqrt{6} |E_{3,4}| + \sqrt{5} |E_{2,6}| + \sqrt{10} |E_{3,6}| \)

= 4p(\sqrt{3}) + 4p(\sqrt{6}) + 4p(\sqrt{5}) + (12pq-10p)(\sqrt{10})

= 4p(\sqrt{3} + \sqrt{5} + \sqrt{6}) + 2\sqrt{10}p(6q-5)

3. Randić indices for 6-layered SW TiO\textsubscript{2} NTs

The graph of 6-layered SW TiO\textsubscript{2} NTs can be viewed as in Fig. 3.1. The 2-parametric chemical graph of 6-layered SW TiO\textsubscript{2} NTs is denoted by TNT\textsubscript{6} [p,q]. It is defined periodically as shown in Fig. 3.1, where p and q are number of titanium atoms in each column and each row respectively.
The graph of 6-layered SW TiO$_2$ NTs

Fig. 3.1. The graph of 6-layered SW TiO$_2$ NTs

The size of TNT$_6$ [p,q] is 20pq + 2p. There are six kinds of edges corresponding to their degrees of end vertices which are

- $E_{2,2} = \{ uv \in E(G) | d_u(G) = 2 \text{ and } d_v(G) = 2 \}$
- $E_{2,3} = \{ uv \in E(G) | d_u(G) = 2 \text{ and } d_v(G) = 3 \}$
- $E_{2,4} = \{ uv \in E(G) | d_u(G) = 2 \text{ and } d_v(G) = 4 \}$
- $E_{2,5} = \{ uv \in E(G) | d_u(G) = 2 \text{ and } d_v(G) = 5 \}$
- $E_{3,4} = \{ uv \in E(G) | d_u(G) = 3 \text{ and } d_v(G) = 4 \}$
- $E_{3,5} = \{ uv \in E(G) | d_u(G) = 3 \text{ and } d_v(G) = 5 \}$

The edge partition of edge set of TNT$_6$ [p,q] along with their cardinalities can be seen in Table 3.1.

<table>
<thead>
<tr>
<th>$E_{d_u,d_v}$</th>
<th>$E_{2,2}$</th>
<th>$E_{2,3}$</th>
<th>$E_{2,4}$</th>
<th>$E_{2,5}$</th>
<th>$E_{3,4}$</th>
<th>$E_{3,5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cardinality of $E_{d_u,d_v}$</td>
<td>2p</td>
<td>2p</td>
<td>6p</td>
<td>8pq</td>
<td>2p</td>
<td>2p(6q-5)</td>
</tr>
</tbody>
</table>

Table 3.1.

Following theorems exhibit the Randić indices for 6-layered SW TiO$_2$ NTs.

**Theorem 3.1.** The general Randić index for 6-layered SW TiO$_2$ NTs is given by

$$R_\alpha(G) = 2^{\alpha+1}p(2^\alpha + 3^\alpha + 3.4^\alpha + 6^\alpha) + 2p5^\alpha (2.3^{\alpha+1}q + 2^{\alpha+2}q - 5.3^\alpha)$$

**Proof.**

$$R_\alpha(G) = \sum_{uv \in E(G)}(d_u(G)d_v(G))^\alpha$$

$$= 4^\alpha |E_{2,2}| + 6^\alpha |E_{2,3}| + 8^\alpha |E_{2,4}| + (10)^\alpha |E_{2,5}| + (12)^\alpha |E_{3,4}| + (15)^\alpha |E_{3,5}|$$

$$= 2p4^\alpha + 2p6^\alpha + 6p8^\alpha + 2p(12)^\alpha + 8pq(10)^\alpha + 2p(6q - 5)(15)^\alpha$$

$$= 2^{\alpha+1}p(2^\alpha + 3^\alpha + 3.4^\alpha + 6^\alpha) + 2p5^\alpha (2.3^{\alpha+1}q + 2^{\alpha+2}q - 5.3^\alpha)$$
Theorem 3.2. The Randić indices of 6-layered SW TiO$_2$ NTs for $\alpha = \frac{1}{2}, -\frac{1}{2}, 1, -1$ are as under

(i). $R_1(G) = RR(G) = [2\sqrt{5}q(3\sqrt{3} + 2\sqrt{2}) + 2 + 2\sqrt{3} + \sqrt{6} + 6\sqrt{2} - 5\sqrt{15}]2p$

(ii). $R_1(G) = \frac{p}{\sqrt{6}}(\sqrt{2} + 2 + \sqrt{6} + 3\sqrt{3} - 2\sqrt{10}) + \frac{4pq}{\sqrt{5}}(\sqrt{2} + \sqrt{3})$

(iii). $R(G) = 2p(130q - 29)$

(iv). $R_{-1}(G) = \frac{p}{60}(96q + 65)$

Proof. (i). $R_1(G) = RR(G) = \sum_{u,v\in E(G)} d_u(G)d_v(G)$

$= \sqrt{4} |E_{2,2}| + \sqrt{6} |E_{2,3}| + \sqrt{8} |E_{2,4}| + \sqrt{10} |E_{2,5}| + \sqrt{12} |E_{3,4}| + \sqrt{15} |E_{3,5}|$

$= 2p\sqrt{4} + 2p\sqrt{6} + 6p\sqrt{8} + 2p\sqrt{12} + 8pq\sqrt{10} + 2p(6q - 5)\sqrt{15}$

$= [2\sqrt{5}q(3\sqrt{3} + 2\sqrt{2}) + 2 + 2\sqrt{3} + \sqrt{6} + 6\sqrt{2} - 5\sqrt{15}]2p$

(ii). $R_1(G) = \sum_{u,v\in E(G)} \frac{1}{\sqrt{d_u(G)d_v(G)}}$

$= \frac{1}{\sqrt{4}} |E_{2,2}| + \frac{1}{\sqrt{6}} |E_{2,3}| + \frac{1}{\sqrt{8}} |E_{2,4}| + \frac{1}{\sqrt{12}} |E_{3,4}| + \frac{1}{\sqrt{15}} |E_{3,5}|$

$= \frac{2p}{\sqrt{4}} + \frac{2p}{\sqrt{6}} + \frac{6p}{\sqrt{8}} + \frac{2p}{\sqrt{12}} + \frac{8pq}{\sqrt{10}} + \frac{12pq - 10p}{\sqrt{15}}$

$= \frac{p}{\sqrt{6}}(\sqrt{2} + 2 + \sqrt{6} + 3\sqrt{3} - 2\sqrt{10}) + \frac{4pq}{\sqrt{5}}(\sqrt{2} + \sqrt{3})$

(iii). $R(G) = \sum_{u,v\in E(G)} d_u(G)d_v(G)$

$= 4 |E_{2,2}| + 6 |E_{2,3}| + 8 |E_{2,4}| + 12 |E_{3,4}| + 10 |E_{2,5}| + 15 |E_{3,5}|$

$= 2p(4) + 2p(6) + 6p(8) + 2p(12) + 8pq(10) + (12pq - 10p)(15)$

$= 2p(130q - 29)$

(iv). $R_{-1}(G) = \sum_{u,v\in E(G)} \frac{1}{d_u(G)d_v(G)}$

$= \frac{|E_{2,2}|}{4} + \frac{|E_{2,3}|}{6} + \frac{|E_{2,4}|}{8} + \frac{|E_{3,4}|}{12} + \frac{|E_{2,5}|}{10} + \frac{|E_{3,5}|}{15}$

$= \frac{2p}{4} + \frac{2p}{6} + \frac{6p}{8} + \frac{2p}{12} + \frac{8pq}{10} + \frac{12pq - 10p}{15} = \frac{p}{60}(96q + 65)$
Theorem 3.3. The reduced reciprocal Randić index for 6-layered SW TiO$_2$ NTs is given by

$$RRR(G) = 2p(1-9\sqrt{2} + \sqrt{6} + 3\sqrt{3}) + 8pq(2 + 3\sqrt{2})$$

Proof. $RRR(G) = \sum_{uv \in E(G)} \sqrt{(d_u(G) - 1)(d_v(G) - 1)}$

$$= |E_{2,2}| + |E_{2,3}| + \sqrt{3} |E_{2,4}| + \sqrt{6} |E_{3,4}| + \sqrt{4} |E_{2,5}| + \sqrt{8} |E_{3,5}|$$

$$= 2p + 2p(\sqrt{2}) + 6p(\sqrt{3}) + 2p(\sqrt{6}) + 8pq\sqrt{4} + (12pq - 10p)(\sqrt{8})$$

$$= 2p(1 - 9\sqrt{2} + \sqrt{6} + 3\sqrt{3}) + 8pq(2 + 3\sqrt{2})$$

4. Conclusion and general remarks

In this paper, we have conducted the study of Randić indices for two types of SW TiO$_2$ NTs: 3-layered and 6-layered SW TiO$_2$ NTs. The Randić index was not only much studied by both chemists and mathematicians but was a subject of a variety of modifications and generalizations. We presented the exact formulae of Randić indices for these SW TiO$_2$ NTs. Various graph-theoretic parameters and certain distance based and counting related topological descriptors for these SW TiO$_2$ NTs are still open problems.

REFERENCES