Original articles

Sorption of 3-glucosides of six common natural anthocyanidins on anatase

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Abstract

In this study, the sorption of 3-glucosides of six common natural aglicones: delphinidin, cyanidin, petunidin, pelargonidin, peonidin and malvidin, on the surface of anatase was studied in comparison with sorption on the surface of silica gel, as a result, a different order of change in the sorption activity of anthocyanins depending on their structure was found. The structure of the (001) face of the surface layer of anatase crystals due to the olation and oxolation of the initial $[Ti(OH)_4(H_2O)_2]$ octahedra upon condensation into three-dimensional grids was proposed.

The mechanisms of sorption of anthocyanins on the surface of sorbents are proposed. Delphinidin derivatives have the highest sorption activity on anatase.

Keywords: Anthocyanins, Sorption, Sorption mechanisms, Anatase, Surface layer structure, Silica gel

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1. Introduction

Dye sensitised solar cells (DSSC) became the focus of attention after the work of Swiss researchers [1], who created a solar battery by a combination of nanostructured electrodes and a dye capable of efficient charge transfer. The use of sintered mesoporous titanium dioxide turned out to be a breakthrough idea that made it possible to lay the foundations for the design of DSSC, raising the efficiency of converting light energy into electrical energy from 1% (for batteries with non-porous TiO_2) up to 7% [2]. The principle of operation of DSSC is as follows [2]:

1) at the anode, the dye captures a light quantum, transiting into an excited electronic state:

$$D + h\nu \rightarrow D^*; \qquad (1)$$

2) the dye in the excited state transfers an electron to the semiconductor (TiO_2), transforming into the corresponding cation:

$$D^* - e^-(TiO_2) \rightarrow D^+; \qquad (2)$$

3) the dye returns to its original state, oxidizing the iodide ion from the electrolyte:

$$2D^+ + 3I^- \rightarrow 2D + I_3^-. \qquad (3)$$

4) the electrolyte is regenerated at the cathode (Pt):

$$I_3^- + 2e^-(Pt) \rightarrow + 3I^-. \qquad (4)$$
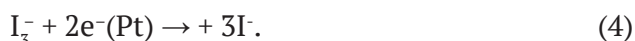
Various natural dyes, including anthocyanins, have been studied as sensitisers for the production of cheap and environmentally friendly DSSC [2–5]. For efficient electron transfer from a dye to a semiconductor, direct chemical bonding between anthocyanins and titanium atoms is required. Two variants of differing schemes were proposed for such binding, shown in Fig. 1. In the first variant, the quinonoid [3], and in the second variant, the flavylium [4] form of anthocyanins are adsorbed, but in both cases the interaction occurs through the B-ring of anthocyanins. At the same time, due to differences in the structure of anthocyanins, the structure of the B-ring should have a decisive influence on binding, and in the case of pelargonidin derivatives, only one-point interaction is possible due to the presence of only one hydroxyl (or keto-group in the quinonoid form) group in the B-ring.

The efficiency of sorption of anthocyanins based on various aglicones on titanium dioxide has not been investigated in any of the studies known to us.

The purpose of this study was the comparison of the sorption of 3-glucosides of six common anthocyanidins (pelargonidin, cyanidin, peonidin, delphinidin, petunidin, and malvidin) on anatase, which is one of the three natural crystalline modifications of TiO_2 used as a semiconductor in solar cells and the comparison with the sorption of the same substances on silica gel.

2. Experimental

Anthocyanins were obtained by extraction with a 0.1 M HCl aqueous solution from plant materials, specifically the leaves of eastern redbud (*Cercis canadensis*) and fruits of common barberry (*Berberis vulgaris*). The resulting extracts were purified by solid-phase extraction using DIAPAC C18 syringe cartridges [5]. Re-extracts were obtained by eluting anthocyanins from the cartridges with a mixture of ethanol and 0.1 M HCl aqueous solution. Ethanol was removed using a vacuum rotary evaporator. The solutions were mixed to obtain a complete set of 3-glucosides of cyanidin, peonidin, delphinidin, petunidin,
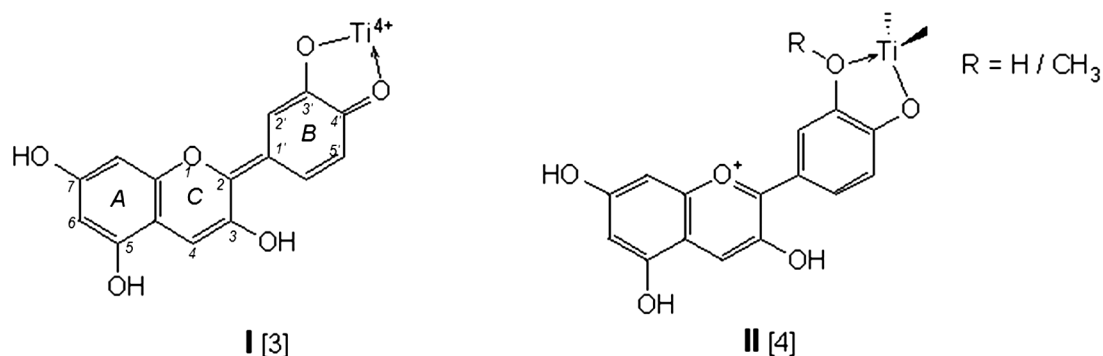

Fig. 1. Anthocyanins bonding with surface Ti atoms according to studies [3] and [4]

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and malvidin from eastern redbud leaves [7] and pelargonidin 3-glucoside from barberry fruits [8] in comparable amounts.

For the sorption of anthocyanins by anatase and silica gel, the same purified extracts or their mixtures were used. Accurate weighed quantities of anatase or silica gel in the amount from 0.2 g to 1.0 g with a step of 0.2 g were added to 10 ml of extracts with a reduced (i.e., taking into account dilution before spectrophotometry) optical density at an absorption maximum of about 2–3. The resulting mixtures were vigorously shaken for at least 2 h, followed by centrifugation for 10 min at 2700 rpm. The mother solution was separated by decantation, and its composition, as well as the composition of the initial extract, was analysed by HPLC [9].

3. Results and discussion

It should be noted that the schemes of interaction between anthocyanins and anatase surface, proposed in the scientific literature and presented in Fig. 1, are not substantiated. Thus, scheme 1 in Fig. 1 suggests the formation of chelate complexes with the participation of the quinonoid structure, although the electronic absorption spectra of anthocyanins in the sorbed state presented in the cited article correspond to the flavylium form. Structure II includes titanium with an oxidation state of +3 with a tetrahedral environment and the flavylium form of anthocyanins in the form of a chelate complex. Pelargonidin derivatives cannot form such complexes, but their inefficiency does not follow from the known literature data (see review [2]).

On the other hand, it is known [10, 11] that the structures of anatase, rutile, and brookite are composed of distorted octahedra, and the only difference is in the joining of these octahedra and in their arrangement in space. At the same time, in [12], a scheme of olation and oxolation for the joining of $[Ti(OH)_4(H_2O)_2]$ or $[Ti(OH)_3(H_2O)_3]^+$ octahedra into bulk crystal structures was proposed. During the olation of two such octahedra along the edges gives rise to two bridging hydroxide ions OH-, and as a result of further oxolation, an oxygen atom with a trigonal environment of titanium atoms arises. Thus, the coordination number of titanium inside the crystals is 6, and the coordination number of oxygen atoms is 3.

A study comparing the sorption propensity of anthocyanins on the surface of anatase was performed in comparison with sorption on the surface of silica gel. The mixture was composed in such a way that the structure of anthocyanins differed in the number of hydrogen bond donors (OH-groups) and hydrogen bond acceptors (as well as electron pair donors for donor-acceptor interaction, OH- and/or OCH_3-groups) in the B-ring. For this, a solution containing 3-glucosides of six main natural anthocyanidins: delphinidin (Dp3Glu, three OH groups in the B-ring), cyanidin (Cy3Glu, two OH groups in the B-ring), petunidin (Pt3Glu, two OH groups and one OCH_3-group in the B-ring), peonidin (Pn3Glu, one OH group and one OCH_3-group in the B-ring) and malvidin (Mv3Glu, one OH group and two OCH_3-groups in the B-ring), and pelargonidin (Pg3Glu, only one OH group in the B-ring) was prepared. The results obtained for anatase and silica gel are presented in Table 1 and Table 2.

The tables show the degree of sorption of each of the anthocyanins (α), relative values of the degree of sorption, calculated using the formula:

Table 1. Parameters of sorption activity of anthocyanins on anatase

No	Anthocyanin	Experiment No. 1			Experiment No. 2			Mean value $\bar{\beta}$
		α	α(rel.)	β	α	α(rel.)	β	
1	Dp3G	0.57	11	24.5	0.74	8.81	31.5	28.0
2	Cy3G	0.28	5.43	7.19	0.45	5.31	8.83	8.01
3	Pt3G	0.37	7.01	10.5	0.55	6.5	13.2	11.8
4	Pg3G	0.05	1	1	0.08	1	1	1
5	Pn3G	0.14	2.65	2.92	0.21	2.53	2.94	2.93
6	Mv3G	0.18	3.38	3.88	0.26	3.11	3.86	3.87

α - absorption degree of the anthocyanin, a(rel.) – ratio to the parameter for Pg3Glu, $\bar{\beta}$ – mean value.

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Table 2. Parameters of sorption activity of anthocyanins on silica

No	Anthocyanin	Experiment No. 1			Experiment No. 2			Mean value $\bar{\beta}$
		α	α(rel.)	β	α	α(rel.)	β	
1	Dp3G	0.42	0.92	0.86	0.47	0.94	0.88	0.87
2	Cy3G	0.43	0.94	0.90	0.47	0.93	0.87	0.89
3	Pt3G	0.45	0.98	0.97	0.51	1.01	1.03	1
4	Pg3G	0.46	1	1	0.5	1	1	1
5	Pn3G	0.5	1.09	1.19	0.55	1.1	1.22	1.2
6	Mv3G	0.51	1.11	1.23	0.59	1.17	1.41	1.32

α - absorption degree of the anthocyanin, a(rel.) – ratio to the parameter for Pg3Glu, $\bar{\beta}$ – mean value.

$$\alpha\left(\text{rel}\right) = \frac{\alpha(i)}{\alpha(\text{Pg\,3\,Glu})}, \qquad (5)$$

and β – sorption parameter calculated using the formula [13]:

$$\beta(i) = \frac{\frac{1}{\alpha(A)} - 1}{\frac{1}{\alpha(B)} - 1} = \frac{b(B)}{b(A)}. \qquad (6)$$

On silica gel, silanol (Si-OH) groups are active and accessible, while siloxane groups are more sterically hindered and are of secondary importance in sorption. The acidity of the surface silanol groups enables their involvement in the formation of hydrogen bonds with the sorbate as proton donors. In this case, the difference in the acceptor capacity (during the formation of a hydrogen bond) of OH- and OCH_3-groups should not be high, with some preference for groups with oxygen atoms with the highest charge.

For the estimation of the charge state of oxygen atoms in anthocyanins, we calculated the distribution of electron density in model 3-methylaglycones using the semi-empirical PM3 method (Table 3).

When 3-glucosides are adsorbed on the acid sites of silica gel, their functional groups can participate in the formation of a hydrogen bond as acceptors for oxygen atoms of the B-ring or A-ring. Based on the comparison of the charges on oxygen atoms, shown in Table 3, it can be assumed that for derivatives of cyanidin, petunidin, peonidin, and malvidin, the hydrogen bond (as an acceptor) should be formed by the oxygen atom of the hydroxyl group in position 4' and in the case of delphinidin it should be formed by the oxygen atom of the hydroxyl group in position 3'.

In the case of a pelargonidin derivative, sorption at position 7 (i.e., in the A-ring) is preferable to sorption at other positions. However, the close values of the parameters of sorption activity of all six anthocyanins (Table 2) on silica gel cannot be explained by the different orientation of anthocyanins relative to the silica gel surface. Obviously, for more stable sorption of anthocyanins, the formation of two hydrogen bonds is necessary. In this case, all six anthocyanins have in common the presence of hydroxyl groups in positions 5 and 7, which have only small differences in charges for all six anthocyanins. In this case, the geometric parameters also turn out to be favourable: the distance between neighbouring silanol groups on the silica gel surface (0.526 nm [13]) is consistent with the distance between the oxygen

Table 3. Distribution of electron density between oxygen atoms in 3-methoxyanthocyanidins

Anthocyanin	The charge on the oxygen atom in position:				
	5	7	3'	4'	5'
3MeDp	−0.181	−0.185	−0.223	−0.203	−0.202
3MeCy	−0.183	−0.186	−0.209	−0.203	−
3MePg	−0.184	−0.187	−	−0.182	−
3MePt	−0.182	−0.187	−0.195	−0.204	−0.202
3MePn	−0.184	−0.188	−0.196	−0.179	−
3MeMv	−0.182	−0.187	−0.195	−0.204	−0.202

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atoms of hydroxyl groups in positions 5 and 7 in anthocyanins (0.476 nm, calculated by the PM3 method); the existing small differences are levelled by the flexibility of the orientation of hydrogen bonds, and the interaction scheme is shown in Fig. 2. Moreover, the anthocyanin plane can be tilted towards the interior of the pattern in a way that the steric effect of the glycosidic substituent at position 3 can be neglected.

A significant difference in the sorption of anthocyanins on silica gel and on anatase becomes apparent when analysing the data in Table 1. The greatest increase in sorption activity is observed with an increase in the number of hydroxyl groups in the sorbate (in the series of pelargonidin - cyanidin - delphinidin derivatives), and also, even though to a lesser extent, in the series of pelargonidin - peonidin - malvidin derivatives.

For the prediction of the possible mechanism of anthocyanin sorption on anatase, it is necessary to know the surface structure of TiO_2, the elementary crystal lattice of which is shown in Fig. 3.

The outer planar octahedral layer of the titanium-oxygen octahedra of the [001] face can be obtained by olation (i.e., combining by a bridging OH group) of $[Ti(OH)_4(H_2O)_2]$ octahedra at which all water molecules are removed, and adjacent octahedra are connected by equatorial bridging OH groups, forming a solid plane, Fig. 4a. In this case, all titanium atoms must contain two axial OH groups to maintain the octahedral coordination:

a) the first octahedral layer (A) after the olation of monomeric octahedra; b) association of two layers of octahedra (A and B) with partial oxolation; c) structure after partial dehydration.

Oxolation during the formation of a three-dimensional grid can occur due to the combination of the upper layer of octahedra (A) with another similar layer (B), Fig. 4b. In this case, based on the elementary crystal cell, the oxo group is formed during the condensation of the bridging (equatorial) OH group of layer A from below with the upper axial OH group of the lower layer B. Similarly (since the octahedra of layers A and B are combined along adjacent opposite edges), additionally oxolation occurs (i.e., the formation of bridging oxo groups) of the lower axial OH groups of layer A with half of the equatorial OH groups of layer B. This leads to distortion of the octahedra due to the displacement of the oxo groups of layer A downwards, while for steric reasons another pair of *trans*-hydroxyl (before oxolation) groups of the upper layer should rise up from the plane. This allows the completion of
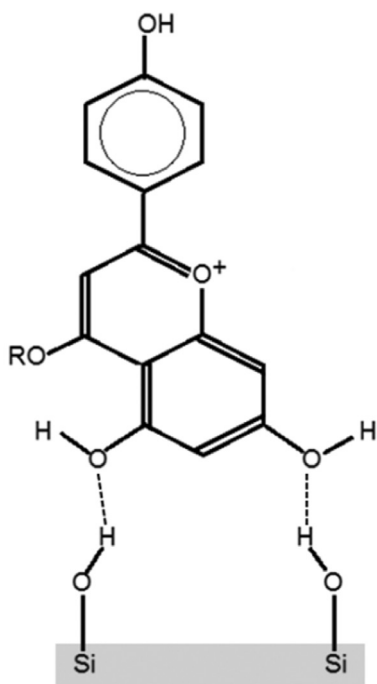

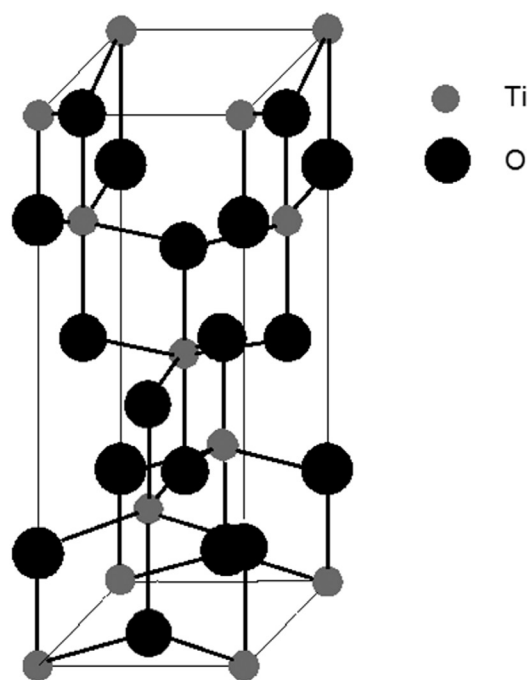**Fig. 2**. Two-point anthocyanin adsorption on the silica surface

Fig. 3. Anatase unit cell

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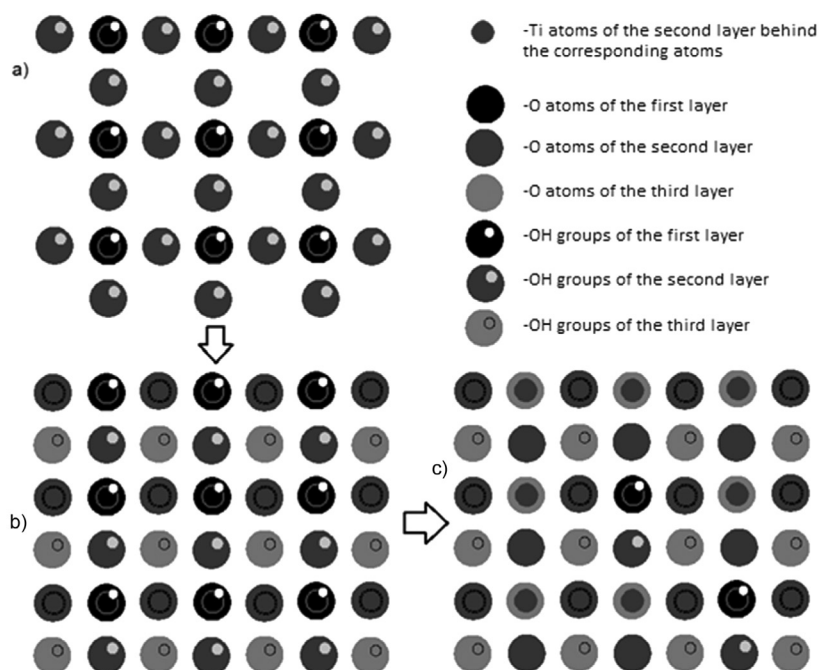

Fig. 4. Formation of the surface layers of the anatase (001) face

the oxolation of layer A from above with the third layer (B) in the formation of a three-dimensional structure.

Without this oxolation, the surface of the [001] face will be represented by titanium atoms containing axial OH groups, ribbons of coordinatively saturated oxo groups shifted downward due to oxolation, and ribbons of OH groups shifted upward and are accessible for sorption with molecules of potential sorbates, Fig. 4b. Due to the steric effect of the inner layers (with complete oxolation and with a shortened distance between titanium atoms), dehydration of the outer layer is possible with the replacement of equatorial OH groups by coordinatively unsaturated oxo groups and with the formation of an axial vacancy in the coordination sphere of the titanium atom, Fig. 4c. Such dehydration and its reverse hydration are reversible, which follows from the data of [14] on the study of X-ray photoelectron spectra of annealed titanium dioxide nanopowder before and after hydration. Indeed, in non-hydrated titanium dioxide, the main band has the lowest energy of 534.0 eV; it is attributed to internal (fully oxolated) oxygen atoms. The oxygen atoms with an energy of about 555.5 eV, which are attributed to oxygen from the surface OH groups, are also quite noticeable.

Their energies noticeably differ from the energy of oxygen atoms of sorbed water molecules with a photon energy of about 537.5 eV. During the hydration of the nanopowder, the concentration of surface hydroxyl groups increased approximately three to four times, confirming the reversibility of hydration-dehydration. However, to obtain effective DSSC, a direct donor–acceptor bond between the coordinatively unsaturated titanium atom on the surface and the oxygen atom of the auxochromic hydroxy or methoxy group of the anthocyanin molecule is desirable. Probably, the formation of an axial vacancy of the titanium atom on the surface is possible during annealing of the initial TiO_2 and explains the need for such a procedure.

As can be seen from the data in Table 1, there is a significant difference in the sorption capacity of anthocyanins depending on the structure of the B-ring. Therefore, it can be assumed that the B-ring with significantly different structure among the six anthocyanins used is responsible for the sorption of anthocyanins on anatase. Moreover, two-point sorption (i.e., the presence of two substituents in the B-ring) is preferable to one-point sorption.

Based on the values of the charges on the oxygen atoms of functional groups, it can be

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assumed that an increase in the charge of the oxygen atom (i.e., its donor properties during the formation of a donor-acceptor bond) enhances sorption in the series of substituted pelargonidin (substitution of the OH group in the 4′ position with a charge on the oxygen atom −0.182) < cyanidin (substitution of the OH group in position 3′ with a charge on the oxygen atom -0.209) < delphinidin (substitution of the OH group in position 3′ with a charge on the oxygen atom −0.223) with the possibility of two-point sorption in the last two cases. Two-point sorption is also possible for petunidin, peonidin, and malvidin derivatives. However, the substitution of the OH group by the OCH_3-group does not contribute to the enhancement of sorption, since the increase of the charge on the oxygen atoms and OH- and OCH_3-groups was practically not observed in the case of the peonidin and malvidin derivatives.

Therefore, delphinidin, petunidin, or cyanidin glycosides can be proposed as being the most effective anthocyanins for the sorption modification of the anatase surface, and the sorption interaction of anthocyanin with the surface can be represented by the diagrams shown in Fig. 5.

In the proposed scheme, the titanium atom completes the coordination sphere with an octahedron due to the donor-acceptor bond with the lone pair of electrons of the OH group in position 3′ (Scheme I), or the OH group in position 4′. It is this bond that is likely to be the main link in the transfer of an electron from anthocyanin to titanium dioxide in solar cells. Additionally, the oxygen atom on the anatase surface forms a hydrogen bond with the hydroxyl group in position 4′ (Scheme I). For the sorption of methoxy derivatives, the donor–acceptor bond with the titanium atom must be performed by the oxygen atom of the OH groups in the 4′ position (Scheme II), and the methoxy groups can enhance sorption due to the formation of a hydrogen bond with bridging hydroxyl groups on the surface. The number of hydroxyl groups is not high, which explains only a moderate increase in the sorption capacity in the case of substituted peonidin and malvidin (compared to pelargonidin derivatives).

3. Conclusions

Thus, the nature of the sorption of 3-glucosides of the six common anthocyanidins on anatase is fundamentally different from the sorption on silica gel. In the first case, sorption is determined by the functional groups of the B-ring, while in the second case, it is determined by the hydroxyl groups of the A-ring. Based on the results of the experiments performed, it can be assumed that delphinidin derivatives should have the highest efficiency as anatase sensitisers.

Author contributions

All authors participated in all stages of the study, preparation and discussion of the results.
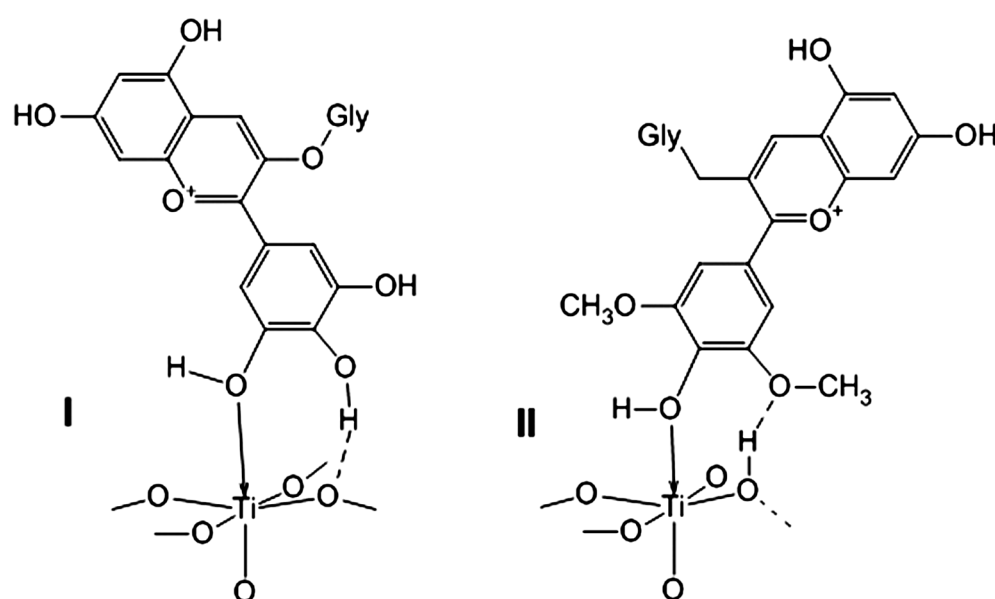

Fig. 5. Schemes of two-point sorption of anthocyanins on the anatase surface

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Conflict of interests

The authors declare that they have no conflict of interest.

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