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Which anthocyanin is the best corrosion inhibitor?

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Abstract. Anthocyanins are one of the major dyes in plants. They have an aromatic and heteroatom within their framework structure so that anthocyanins are likely to be bound to metal surfaces via heteroatoms or π - π interactions. This property leads to the potential application of anthocyanins as corrosion inhibitors. However, there are challenges in determining the best anthocyanin for corrosion inhibitors due to the structure of anthocyanins are closely similar. The understanding of the corrosion inhibitor donor-acceptor properties is the simplest method to predict the corrosion inhibition performance of the targeted compounds. Therefore, the aim of this research is to predict the best anthocyanin for corrosion inhibition in the term of their electron transfer ability. The study presented the structures, the frontier molecular orbitals and the donor acceptor map of anthocyanins as corrosion inhibitor. A density functional theory at B3LYP level of calculation was performed systematically in an attempt to predict the corrosion inhibition properties based electron transfer ability of the ten well known anthocyanins: cyanidin (CN), aurantinidine (AU), delphinidine (DP), eropinidine (EU), luteonidine (LT), pelargonidine (PL), malvinidine (MV), peonidine (PE), petunidine (PT), rosinidin (RS). The theoretical prediction suggested that the corrosion inhibitor performances followed the order of DP > EU > CY > PT > MV > PE > RS > LT > AU > PL. The DP molecule has more number of hydroxyl (OH) groups than other anthocyanins, so that DP transfers more electrons to form stronger bonds with metals. The study will contribute to the design of new high inhibition efficiency of anthocyanin-based corrosion inhibitor.

Keywords: anthocyanin, corrosion inhibition, density functional theory.

1. Introduction

Anthocyanins are one of the most abundant secondary metabolic compounds that act as color pigments in plants. These compounds are responsible for the blue, red, purple, and yellow colours in the plants flowers and fruits. The main sources of anthocyanins are vegetables and fruits such as tomatoes, red onion, mangosteen, mango, black rice, oranges, apples, eggplants, dragon fruit, and grapes [1-4]. Anthocyanins have 15 carbon atoms in the skeletal structure, arranged in an aromatic pattern, plus some hydroxyl groups, methyl groups, and additional of aromatic groups. With such structures, anthocyanins have a large ability of being strongly bonded to metal surfaces via oxygen heteroatom and π - π interactions. Therefore, anthocyanins may act as excellent corrosion inhibitors due to most of the efficient organic inhibitors contain electronegative functional and π -electron in multiple bonds [5, 6]. These types of functional groups facilitate the formation of complexes between organic inhibitors and



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metal surfaces via a chemical adsorption or physical adsorption [7]. The complex formation between organic inhibitors and metal surfaces creates a highly ordered film on the metal surface and it creates barrier from corrosive medium [8, 9].

Anthocyanins are one of the potential candidates for the green corrosion inhibitor. However, there are challenges in determining the best anthocyanin for corrosion inhibitors due to the structure of anthocyanins are closely similar. More than 500 different types of anthocyanins have been isolated and all are almost similar in structures (Fig. 1). The efficient solution to determine the best anthocyanins based corrosion inhibitors is the application of theoretical studies. The understanding of the corrosion inhibitor donor-acceptor properties is the simplest method to predict the corrosion inhibition performance of the targeted compounds [10, 11]. Therefore, in this work, theoretical investigation was applied in an attempt to establish a hierarchy of the most efficient anthocyanins for corrosion inhibitors. The present study will focus on the ten most popular anthocyanins, namely cyanidin, aurantidin, delphinidin, eropinidin, luteonidin, pelargonidin, malvinidin, peonidin, petunidin, rosinidin.

2. Computational procedure

The geometry of anthocyanins was optimized by density functional theory method at the theory level of B3LYP/6-311G (d,p). The polarized continuum model was used to calculate the solvent effects due to corrosion dominantly occurred in the aqueous environment. To assess the electron donor-acceptor of anthocyanins, the re-optimization of the structure was not performed on the solvent because it had little effect on the energetic so that it was sufficient to use single point calculations on gas-phase geometries [12-14]. All theoretical calculations are performed with the Gaussian 03 package [15]. The quantum chemical parameters (E_{HOMO}), the energy of the lowest molecular orbitals (E_{LUMO}), ionization potential (I), electron affinity (A), the chemical hardness (η), the fraction of electron transferred (ΔN) were calculated [16-19]. The electron donating power (ω^-), electron accepting power (ω^+), the electron accepting index (Ra) and the electron donating index (Rd) was also useful, calculated using previously defined tool [19-21].

3. Result and Discussion

The schematic structures of the studied anthocyanins are depicted in Fig. 1. Anthocyanins have 15 carbon atoms in their main framework with three aromatic rings and additional of heteroatom groups in the form of hydroxyl and methoxy groups. These aromatic rings and functional groups allow the anthocyanins to be strongly bound to the metal surface. These properties lead in anthocyanins having high potential for inhibiting corrosion.

As a consequence of using the DFT method to study the corrosion inhibition properties of anthocyanins, it is important to validate the level of theory being used. Table 1 shows the comparison of the anthocyanins geometry parameters of experimental with theoretical DFT at the level of B3LYP/6-311G (d,p). The geometrical structure of theoretical calculation agrees with the X-ray structure from experimental data of cyanidin [22]. The theoretical bond length of C1-C2, C3-O18, O19-H29 were 1.419 Å, 1.353 Å, 0.969 Å whereas the experimental bond length was 1.413 Å, 1.345 Å, and 0.910 Å. The similar trend was shown by the theoretical and experimental bond angle of C6-C1-C2, C12-C13-C14, C8-C9-C11 were 121.70°, 120.42°, 128.87° and 122.1°, 120.90°, 129.2°, respectively. It showed that the B3LYP/6-311G (d,p) can be applied in the studied systems due to it is sufficient in accuracy and efficient in calculation time.

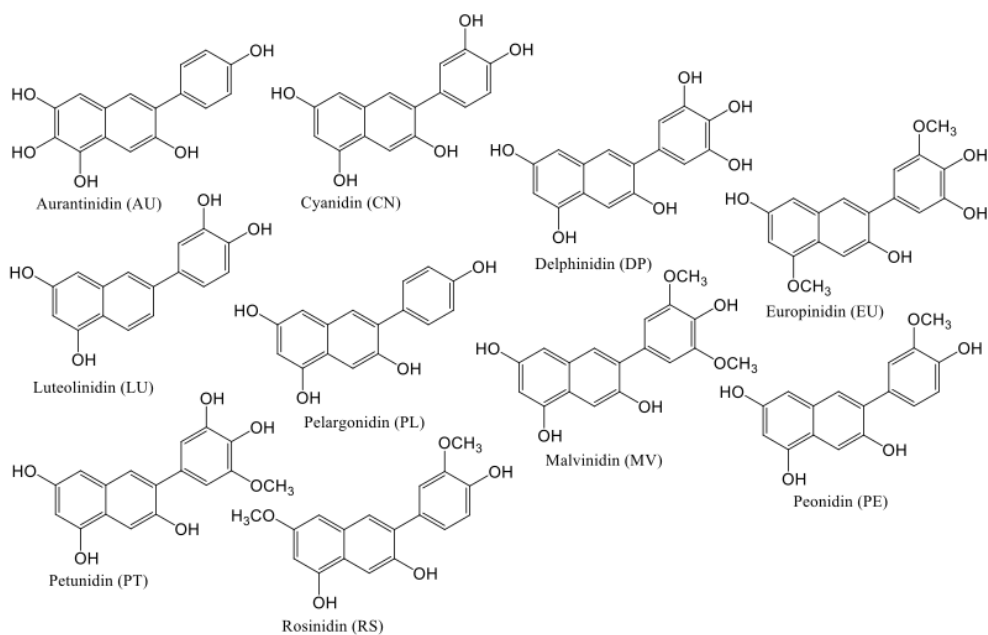


Figure 1. The structures of the studied anthocyanins.

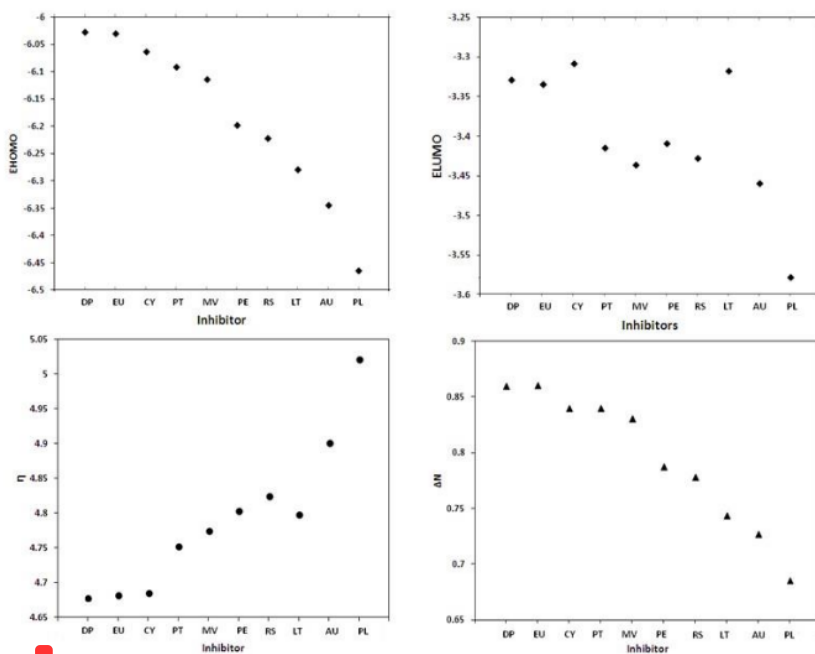


Figure 2. The high occupied molecular orbitals (HOMO) energies and low unoccupied molecular orbital (LUMO) energies, the hardness (η) properties, the number of electrons transferred (ΔN) of anthocyanins determined by B3LYP/6-311G (d,p) level of theory

Table 1. Geometrical parameters of the cyanidin at B3LYP/6-311G(d,p) level of theory

Bond Lengths	Theory	Exp	Bond Angles	Theory	Exp
C1-C2	1.41952	1.413	C6-C1-C2	121.7047	122.1
C2-C3	1.38418	1.366	C1-C2-C3	119.9843	120.0
C3-C4	1.43251	1.432	C2-C3-C4	120.1027	120.0
C4-C5	1.41458	1.408	C3-C4-C5	117.7633	117.1
C5-C6	1.39403	1.376	C4-C5-C6	123.3071	124.1
C6-C1	1.40414	1.387	C5-C6-C1	117.1380	116.7
C5-O10	1.36083	1.361	C5-C4-C7	118.0249	118.4
O10-C9	1.35307	1.349	C4-C7-C8	121.2646	121.3
C9-C8	1.42851	1.396	C8-C9-O10	119.4791	118.4
C8-C7	1.38899	1.380	C9-O10-C5	125.1583	123.7
C7-C4	1.41008	1.382	C16-C11-C12	118.4719	118.9
C8-O19	1.35927	1.351	C11-C12-C13	120.7542	119.9
C3-O18	1.35325	1.345	C12-C13-C14	120.4281	120.9
C1-O17	1.34786	1.336	C13-C14-C15	119.4803	119.5
C9-C11	1.44057	1.453	C14-C15-C16	120.4055	120.4
C11-C12	1.42332	1.404	C15-C16-C11	120.4601	120.3
C12-C13	1.38957	1.383	C1-O17-H27	111.2816	110.0
C13-C14	1.40269	1.378	C9-C11-C16	118.9726	119.4
C14-C15	1.42708	1.400	C1-C2-H22	118.1666	118.0
C15-C16	1.38064	1.371	H22-C2-C3	121.8491	122.0
C16-C11	1.42999	1.409	C2-C3-O18	124.2744	125.2
C14-O21	1.33883	1.352	C3-O18-H31	110.7954	110.0
C15-O20	1.36743	1.355	C3-C4-C7	124.2118	124.5
O17-H27	0.96957	0.890	C7-C8-O19	122.3331	122.4
O18-H31	0.96972	0.790	O19-C8-C9	118.1878	118.1
O19-H29	0.9695	0.910	C8-C9-C11	128.8755	129.2
O21-H28	0.97392	0.820	C9-C11-C12	122.5556	121.8
O20-H32	0.96796	1.020	C11-C12-H24	120.3349	118.0
C2-H22	1.08748	0.940	C12-C13-H25	121.1005	119.0
C6-H23	1.08626	1.090	H26-C16-C11	120.0162	122.0
C7-H30	1.08853	0.950	C14-O10-H28	109.4887	112.0
C12-H24	1.07984	0.970	O21-C14-C15	120.5341	116.3
C13-H25	1.08624	1.000	C14-C15-O20	113.7693	114.7
C16-H26	1.08597	0.970	H32-O20-C15	111.6530	110.0

Fig. 2 shows the high occupied molecular orbitals (HOMO) energies and low unoccupied molecular orbital (LUMO) energies which are related to the reactivity of the anthocyanins. Fig. 3 shows the

optimized geometries and HOMO-LUMO orbitals of anthocyanins. The HOMO energy indicates the tendency of molecules to donate electrons [23]. It is found that delphinidin (DP) has the highest HOMO energy and Pelargonidin (PL) has the lowest HOMO energy. Therefore, DP is more intent on donating electrons than other anthocyanins. This trend can be used as a preliminary prediction that DP has higher corrosion inhibition efficiency.

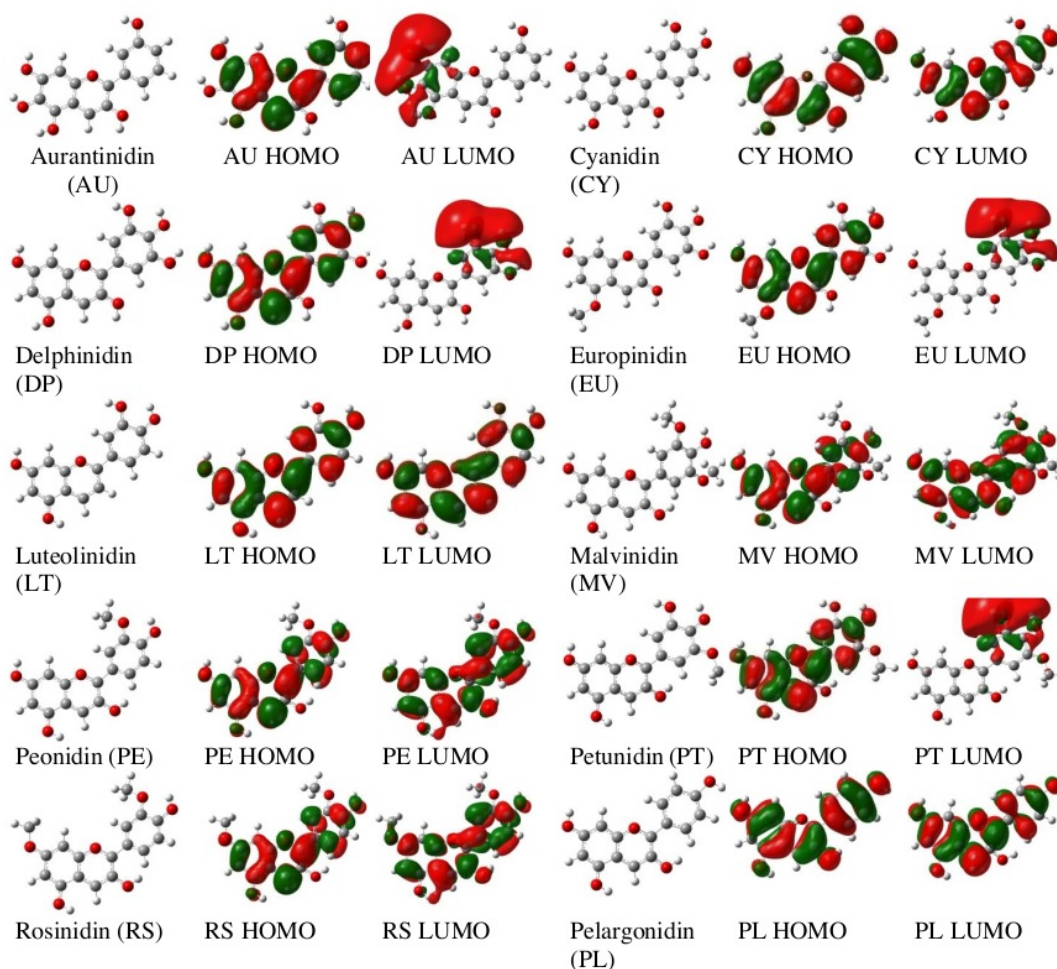


Figure 3. Optimized geometries and contour of HOMO-LUMO orbitals of anthocyanins.

Hard-soft-acid-base (HSAB) properties can be used to predict bonding tendencies between inhibitors and metal atoms. In general, the HSAB rules are hard to interact with hard bases and soft acids preferably interact with soft bases. Metal atoms are known to be soft bases, and so hard base inhibitors are less effective for interacting with metal atoms [23]. Table 2 also shows the value of the hardness (η) properties of the inhibitors. The molecules with the greatest hardness (η) value have the lowest inhibitor efficiency. From Fig. 2, it can be observed that the DP has the lowest hardness value, and the sequence of hard properties is DP > EU > CY > PT > MV > PE > LT > RS > AU > PL. It is expected that DP has the highest corrosion inhibitor efficiency.

The number of electrons transferred (ΔN) is also shown in Fig. 2. Based on Lukovits's study [24], if the ΔN value < 3.6 , the efficiency of the inhibitor will increase due its donating of electrons to the metal surface. The greater the value of ΔN , the greater the ability of the inhibitor to donate electrons to the metal surface. This shows that the DP heteroatom has the highest fraction of electrons transferred, and this is associated with the highest inhibitor efficiency, whereas PL has the fewest fractions, and this is associated with the least inhibitor efficiency. The number of the electrons transferred (ΔN) indicates that the DP has the ability to inhibit corrosion better than other anthocyanins. DP molecule has more hydroxyl (OH) groups than other anthocyanins, therefore DP transfers more electrons to form stronger bonds with metals. In contrast, PL has the lowest OH group so that it is expected that PL will interact weakly with metal surface. In addition, additional methoxy (OCH₃) groups in anthocyanins (in PT, EU, MV, PE, and RS) did not contribute greatly to the electron transfer of anthocyanins, methoxy acts as an electron-attracting group.

Table 2. The ionization potential, electron affinity, electron donating and accepting power, Ra and Rd index in aqueous phases, determined using B3LYP/6-311G(d,p) level of theory

	I (eV)	A (eV)	(electron donating power) ω^-	(electron accepting power) ω^+	Ra	Rd
DP	6.0270	3.3284	10.6162	5.9384	1.7465	3.0682
EU	6.0284	3.3344	10.6444	5.9629	1.7538	3.0764
CY	6.0618	3.3358	10.6192	5.9203	1.7412	3.0691
PT	6.0899	3.4142	10.9830	6.2309	1.8326	3.1742
MV	6.1127	3.4357	11.0688	6.2945	1.8513	3.1990
PE	6.1965	3.4087	10.8494	6.0466	1.7784	3.1356
RS	6.2207	3.4275	10.9184	6.0942	1.7924	3.1556
LT	6.2776	3.3178	10.6310	5.5632	1.7636	3.0994
AU	6.3432	3.4591	10.9597	6.0585	1.7819	3.1675
PL	6.3655	3.4740	11.4256	6.4049	1.8838	3.3021

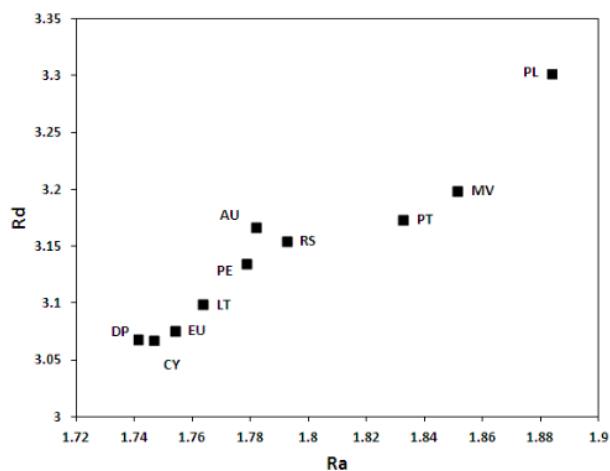


Figure 4. Donor-acceptor map of anthocyanins determined using B3LYP/6-311G(d,p) level of theory.

The ionization potential energy of anthocyanins is shown in Table 2. Ionization energy describes the reactivity of atoms and molecules. High ionization energy indicates that the molecule is inert or stable [23]. Small ionization energy shows more reactive molecules that show the high inhibition efficiency. The smallest ionization energy is shown by DP (6.027 eV) which means it is easier to interact with metals so that it is predicted to inhibit corrosion better than other anthocyanins.

The mechanism of interaction between inhibitors and metals does not only involve donations of electrons from inhibitors to metal but also the presence of back donations from metals to inhibitors, although the amount of donations is small. The ability to accept electrons can be tested by measuring electron affinity (A). Molecules with high and positive electron affinity values have a greater capacity to accept electrons. This molecule will more easily accept electrons from metal so that better interactions occur [23]. Table 2 indicates that PL has the capacity to accept electrons compared to other anthocyanins. However, the capacity to accept these electrons is still less than its ability to donate electrons. It explains why PL is predicted to have the lowest corrosion inhibition performance.

The ability of a molecule to donate and withdraw charge is described simply using a charge transfer model in the form of electron donating and electron accepting power [25]. Molecules with low electron donating power will have the capacity to donate more charges. For electron accepting power cases, lower value of electron accepting power implies lower capacity for accepting electrons. Table 2 shows that the DP has the lowest electron donating power value. The order of increasing electron donating power is DP > CY > EU > LT > PT > PE > RS > AU > MV > PL. This means that the DP has the capacity to transfer the highest charge toward metal, whereas PL is the lowest.

Corrosion generally occurs quickly in acidic conditions. Anthocyanin itself is positively charged in an acidic environment [26]. Positively charged anthocyanin was used in this study because the influence of acid solution on the corrosion process was considered. Table 2 shows the values of Ra and Rd from positive anthocyanins in water solvents. Ra is the electron accepting index and Rd is the electron donating index. The detail equation for Ra and Rd can be seen in Martínez *et al.* [20] and Martínez *et al.* [21]. Schematically a plot of Rd vs. Ra provides an acceptor map of anthocyanin as depicted in Fig. 4. Donor acceptor map (DAM) indicates that anthocyanins are good inhibitor compounds because they act as donors and acceptor electrons simultaneously. Anthocyanins tend to be better electron acceptors than electron donors. Based on DAM data, delphinidin is recommended as the best corrosion inhibitor.

4. Conclusion

The main conclusion of this study is that anthocyanin is a good corrosion inhibitor. It is capable of receiving and also donating electrons simultaneously. Frontier molecular orbital studies, chemical hardness, ionization potential, electron affinity, transferred fraction of electron, the electron donating-accepting power, and donor-acceptor map showed that the best corrosion inhibitor was delphinidin (DP). The sequence of corrosion inhibitor performance of ten studied anthocyanins was delphinidin > europinidin > cyanidin > petunidine > malvinidin > peonidin > rosinidin > luteolinidine > aurantinidine > pelargonidin. This study contributes to the search for new anthocyanin-based corrosion inhibitors.

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