Role of Functional Groups in Selective Adsorption of Gold over Copper Cyano complexes by Activated Carbon: A DFT Study

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Article Info

Abstract

The adsorption of gold and copper cyanide complexes on the activated carbon is investigated using the Density Functional Theory (DFT). In order to represent the activated carbon, two fullerene-like model (presenting structural defect sites) and a simple graphene layer containing different functional groups (presenting chemical active sites) are employed. The structural defect sites show a much lower adsorption tendency toward all the cyano complexes comparing to the chemical active sites. The interaction energy for all of the complexes with structural defect sites (concave) is very low. However, the graphene layer with unsaturated active sites displays the highest level of interaction almost for all the complexes except Cu(CN)4-3. The effect of oxygen functional groups on the graphite edges shows a crucial role in the selectivity of gold adsorption over copper complexes. It has increased adsorption energy for Cu(CN)2- in the presence of OH and COOH, and has decreased adsorption energy for Au(CN)2- by OH and increased by COOH. The study results elucidate the lower selectivity for adsorption of gold over copper cyanides by high oxygen content activated carbon. The energy levels of the HOMO and LUMO orbitals show adsorption of unpaired cyanide anions on the activated carbon surface occurs by electron transfer from the complex to the adsorbent and adsorption onto the activated carbon edges by transferring electrons from the absorbent to the complex. The result has clearly demonstrated that the functional groups increase the adsorption tendency for both the gold (only COOH) and copper complexes (OH and COOH) but deteriorate the selectivity of gold over copper cyanides.

1. Introduction

The adsorption of gold cyanide on the activated carbon is an essential unit operation for extracting gold from ores using the CIP/CIL processes [1]. The adsorption mechanism of gold and copper complexes (the dominant competing species [2]) on the activated carbon is of significant interest as a better understanding of selective adsorption of aurocyanide over other complexes would result in developments in activated carbon preparation and selection [3] as well as optimization of the operating parameters [4]. Despite many experimental studies devoted to provide an insight into the actual mechanism of metal cyanide adsorption on activated carbon, such a mechanism has still remained unresolved [3, 5].

Several mechanisms have been proposed regarding the nature of aurocyanide adsorption on the activated carbon [3] including electrostatic, ion and non-ion pair attraction [3, 5, 6], while copper complexes have received almost no attention [4]. It has been supported by many researchers that aurocyanide irreversibly adsorbs as an unpaired anion $Au(CN)_2^-$ via electrostatic interactions on the active surface sites having polar character, while less active sites are occupied by ion-paired neutral molecular $M^{+n} (Au(CN)_2)_n$ through Van der Waals forces [7]. Copper forms the three different complexes of $Cu(CN)_2^-$, $Cu(CN)_3^{-2}$, and $Cu(CN)_4^{-3}$ with cyanide according to the free cyanide concentration and the pH of the solution [8]. $Cu(CN)_2^-$ is the only species that adsorbs on the

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surface of activated carbon [9]. It has been reported that the adsorption of $Cu(CN)_2^-$ complex on carbon is so stronger than the gold complex that stripes the previously adsorbed gold from activated carbon surface [2]. The adsorption of metal-cyanide species on the activated carbon occurs selectively [10]. In the recent experimental as well as computational modelling studies, this effect has been attributed to the differences in the hydration levels of the metal-cyanide molecule [11, 12].

The reactivity of activated carbon is strongly related to its functional groups [13]. The highest selectivity of gold over copper complexes has been achieved using the activated carbon with the lowest density of surface functional groups that support the industrial application of such activated carbons such as coconut shell [4]. It has been hypothesized that different preferential sites are responsible for adsorption of gold (graphitic planes) and copper (surface edges) [4]. The excessive oxygenated groups like carboxyl and phenolic acid groups reduce the affinity of activated carbon to the gold complex [6]. Also it has been reported that the density of oxygen functional groups negatively affects the gold adsorption onto activated carbon [14]. In another study, four different types of activated carbons containing different densities of functional groups (carboxyl, lactone, phenol, and basic groups) have been examined, and it has been shown that the activated carbon with a lower density of functional groups and relatively higher crystalline character achieves a higher adsorption of gold and a lower adsorption of copper. However, the role of different functional groups has not been clearly defined in this study [4].

Although it is accepted that gold adsorption is associated with the specific functional groups on the carbon surface [15], in the study by Yin and co-workers [3], as the only molecular modelling study on the adsorption mechanism of gold cyanide onto activated carbon, the role of functional groups has been overlooked to simplify the calculations, and only structural defects have been taken into account. Their results illustrate a tendency for aurocyanide to adsorb on the carbon sheet defects (concaves) or edges rather than on the basal plane. Also copper complexes have not been deliberated in this investigation. Therefore, the main objective of this study is to establish the role of surface functional groups and the preferred adsorption sites on the surface of activated carbon using the ab initio DFT simulations. Both the gold and copper cyanide complexes have been examined, and their interactions with different structural defects as well as several surface functional groups located on the planar surface have been calculated and compared. The results have been used to shed light on the mechanism of metal cyanide adsorption on the activated carbon surface. The outcome of this research work can be effectively used to optimize the selective adsorption of gold cyanide onto activated carbon in copper bearing gold ores as well as elution of copper and gold loaded activated carbon.

2. Materials and Methods

DFT calculations have been carried out using the $Dmol^3$ module implemented in the Accelerys Materials Studio software (version 2017). The copper and gold complexes as well as activated carbon were modelled using the generalized gradient functional BYLP (exchange functional Becke combined with the Lee–Yang–Parr nonlocal correlation functional) using an Octa-core desktop PC. A double numerical basis set was applied including two atomic orbitals for each occupied orbital for all atoms plus a p-function polarization on hydrogen atoms (DNP) to represent hydrogen bonding [16]. The convergence criteria for geometry optimizations are summarized in Table 1.

Table 1. Convergence tolerances for geometry optimization calculations.

Convergence tolerance parameters	Tolerances
Maximum displacement	5×10^{-4} Å
Maximum force	2×10^{-4} hartrees/Å
Energy	1×10^{-6} hartrees
	10^{-7} hartrees
Self-consistent field (SCF)	10^{-6} hartrees only for pentagon fullerene -like model
Smearing	No
Orbital cut-off	5.0 Å

No pseudo-potentials or effective core potentials were utilized in this study, and all the results are based on the ''All Electron Relativistic'' calculations. To represent the local environment, calculations are performed using the continuum solvation model, namely COSMO (COnductor like Screening MOdel) [17]. The dielectric constant of water (78.54) was used to outline the solutions in COSMO, presuming a very dilute media with minor dielectric constant deviation from pure water. Multipolar expansion was used for calculation of the solvation energy for all of the models.

The recent studies have shown that microporous carbon has a fullerene-like structure with possible pentagonal arrangement of carbon rings with nonplanar surfaces [18, 19]. This structure has been successfully used by other researchers to represent the microporous carbon structure [3, 20]. Here, the fullerene-like model has been applied by integrating convex, concave, as well as graphene layer to evaluate the active sites on the adsorption of gold and copper complexes. Also to take into account the role of surface groups, different functional groups of OH, COH, and COOH were added to the active sites of the graphene layer in the predefined locations. To represent the cyanide complexes, unpaired anions of $Au(CN)_2^-$, $Cu(CN)_2^-$, $Cu(CN)_3^{-2}$, and finally $Cu(CN)_4^{-3}$ have been used instead of paired neutral complexes to evaluate the electrostatic interaction with very active sites of the activated carbon including unsaturated sites as well as functional surface groups [7].

The adsorption energy of species on activated carbon has been calculated based on the difference between the SCF energy of combined located complex on the surface of activated carbon/activated carbon and individual activated carbon as well as complex (gold or copper cyanide) in $kcal.mol^{-1}$:

$$E_{ad} = E_{complex/activated\ carbon} - (E_{complex} + E_{activated\ carbon}) \quad (1)$$

where $E_{complex/activated\ carbon}$, $E_{complex}$, and $E_{activated\ carbon}$ are the total energies of the combined optimized auro or cuprous cyanide on the activated carbon, the optimized isolated auro or cuprous cyanide, and the optimized isolated activated carbon. The higher negative amounts of adsorption energy indicate favorable and stronger adsorption compared to positive or lower negative values [12].

3. Results and Discussion
3.1. Modeling activated carbon surface

The optimized geometry of the Fullerene-like pentagon model utilized to represent the concave/convex carbon surface is presented in Figure 1.a. The Fullerene-like models, as used by other researchers, are completely saturated with hydrogen with no unsaturated active sites. To represent the chemical active sites, a simple model consisting of single layer with four graphene rings was used [21-27] and some of the edge atoms on the upper side of the graphene layer were unsaturated. Also to evaluate the effect of functional groups, OH, COH or COOH group was settled in one of activate sites of the graphene layer, resulting in the geometries of Figures 1.d to 1.f.

3.2. Effect of structural defects

The interaction between metal cyanide complexes and the concave surface of activated carbon was evaluated. The complexes are almost parallel to the concave with minimal reorientation of the complex structure. It is interesting that the optimized geometry for convex structure could not be achieved as the complex rotated to the other side of the structure (concave) after optimization, supporting the very low interaction energy for convex structure reported by Yin and co-workers [3].
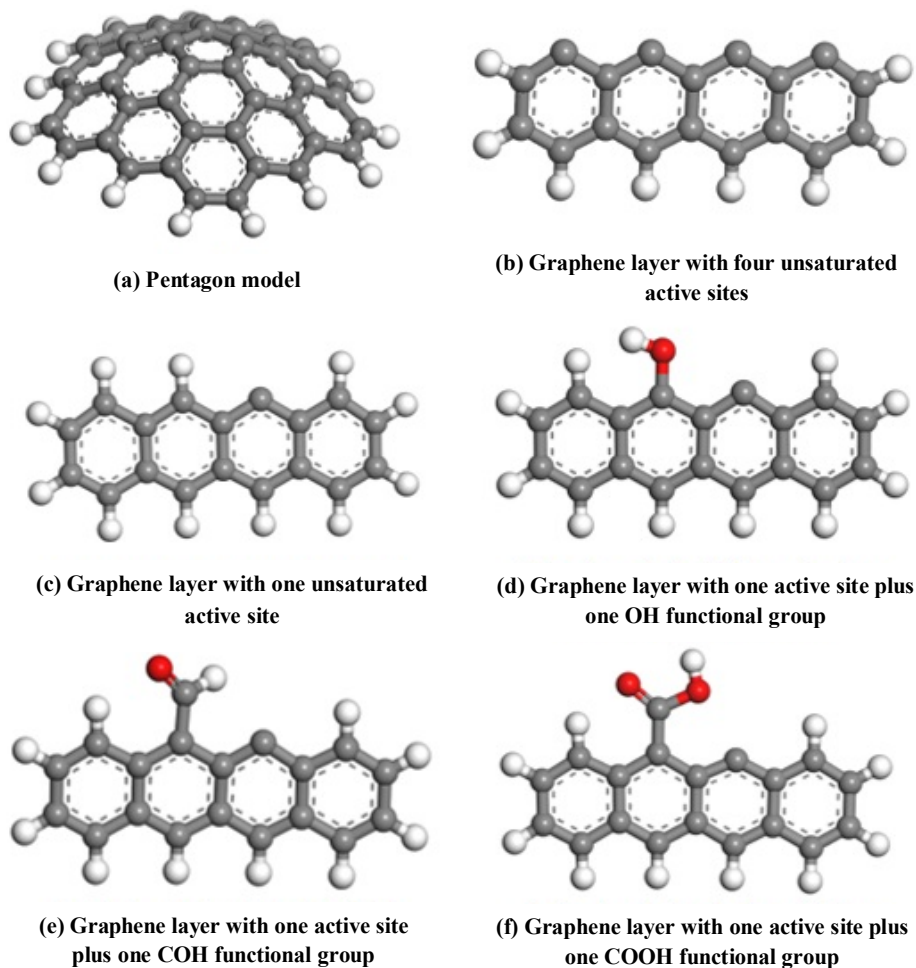
(a) Pentagon model

(b) Graphene layer with four unsaturated active sites

(c) Graphene layer with one unsaturated active site

(d) Graphene layer with one active site plus one OH functional group

(e) Graphene layer with one active site plus one COH functional group

(f) Graphene layer with one active site plus one COOH functional group

Figure 1. Models used in this research work to study adsorption on activated carbon (gray: carbon, red: oxygen, and white: hydrogen).
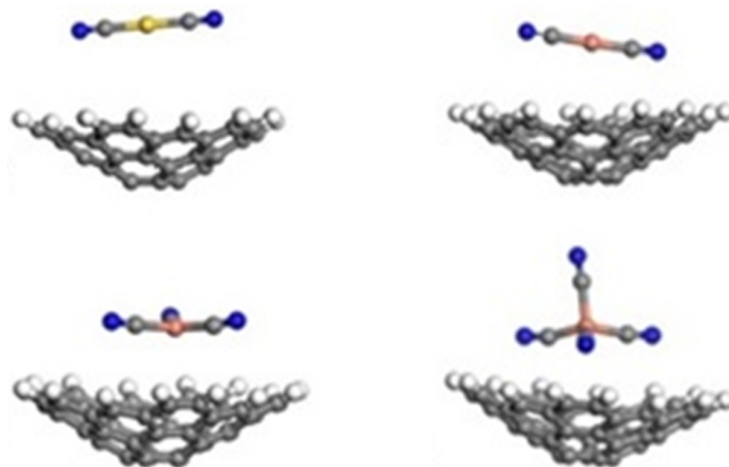

Figure 2. Optimized geometry of gold and copper complexes on surface of fullerene-like pentagon model (yellow: gold, redsphalon: copper, gray: carbon, blue: nitrogen, red: oxygen, and white: hydrogen).

The interaction energy of the four studied complexes with structural defect site of activated carbon is presented in Table 2. The interaction energy for all of the complexes is low with a very high positive adsorption energy for $Cu(CN)_3^{-2}$ and $Cu(CN)_4^{-3}$. The low adsorption energy for dicyano complexes are in agreement with the previous studies that suggest that unpaired cyanide complexes are not adsorbed on the low active sites [5]. However, the order of the complexes in the table is in full agreement with the previously reported data based on the hydration order of the complexes [3, 11].

3.3. Effect of active site

To evaluate the effect of unsaturated edges, the four rings single graphene layer with four unsaturated active sites was examined against each

cyanide complex. The optimized geometry of the structures as well as the interaction energy with cyanide complexes have been demonstrated in Figure 3 and Table 3. In all of the species except $Cu(CN)_4^{-3}$ the central metallic ion has been oriented to the active site, while in $Cu(CN)_4^{-3}$, three of the four nitrogen atoms have been stretched toward the active negative sites.

Table 2. Adsorption energy of gold and copper cyanide complexes with concave surface of activated carbon.

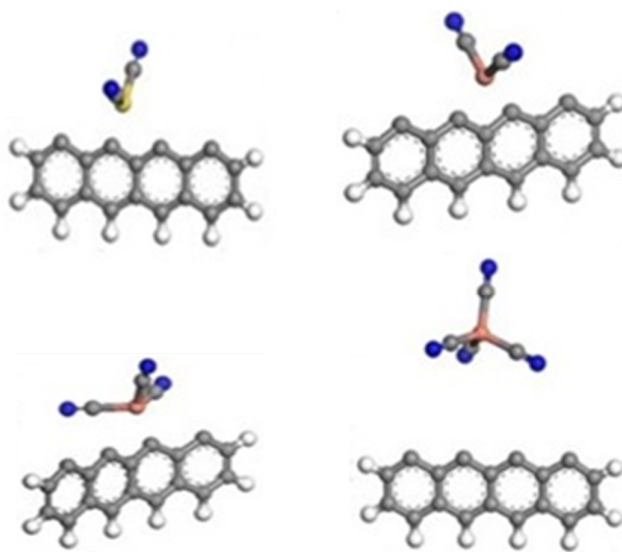| Cyanide complex	Adsorption energy (kJ/mole)
$Au(CN)_2^{-1}$	-27.16
$Cu(CN)_2^{-1}$	-12.68
$Cu(CN)_3^{-2}$	23.10
$Cu(CN)_4^{-3}$	74.00

Figure 3. Optimized geometry of gold and copper cyanide complexes and graphene model with four active site (yellow: gold, redsphalon: copper, gray: carbon, blue: nitrogen, red: oxygen, and white: hydrogen).

Table 3. Adsorption energy of gold and copper cyanide complexes with graphene edges.

Cyanide complex	Adsorption energy (kJ/mole)
$Au(CN)_2^{-1}$	-110.10
$Cu(CN)_2^{-1}$	-87.00
$Cu(CN)_3^{-2}$	84.01
$Cu(CN)_4^{-3}$	64.80

Here, the dicyano complexes demonstrate again the highest interaction with graphene edges similar to the surface defect; however, the amount of interaction is much higher (four times higher for $Au(CN)_2^-$, and 7 times higher for $Cu(CN)_2^-$). The higher amount of interaction energy supports the

hypothesis that more active sites are responsible for the unpaired anions [5]. Also the very distorted structure of dicyano complexes might be an indication for the instability of cyanide complex and possible deposition as metallic cation as reported before by several researchers [1]. Another interesting effect is the higher interaction of $Cu(CN)_4^{-3}$ comparing to $Cu(CN)_3^{-2}$. This effect can be attributed to the different orientation of the structure as in all of the complexes the interaction occurs between the central metallic cation and the active edges, while in $Cu(CN)_4^{-3}$, nitrogen atoms are oriented toward the surface. Apparently three nitrogen atoms have compensated the force

between negative carbon and active sites, so a lower repulsive interaction has been resulted. As presented in the next section, by decreasing the number of unsaturated sites, the interaction energy also declines (from -110.10 to -12.37 $kJ.mol^{-1}$ for $Au(CN)_2^-$ on the four and one unsaturated active sites of graphene layer, respectively).

3.4. Effect of functional groups

To evaluate the role of the functional groups, the three OH, COH, and COOH functional groups were located on one of the active edges of the single layer graphene with another unsaturated active site. The three $Au(CN)_2^-$, $Cu(CN)_2^-$, and $Cu(CN)_3^{-2}$ were examined against the functional group containing graphene layer as well as one unsaturated graphene layer without functional group for comparison purposes. The optimized geometry and interaction energies of the structures have been presented in Figure 4 and Table 4. It has to be noted that $Cu(CN)_4^{-3}$ was not considered in this part of the analysis as no tendency for $Cu(CN)_4^{-3}$ was expected to occur on the surface of graphene layer.
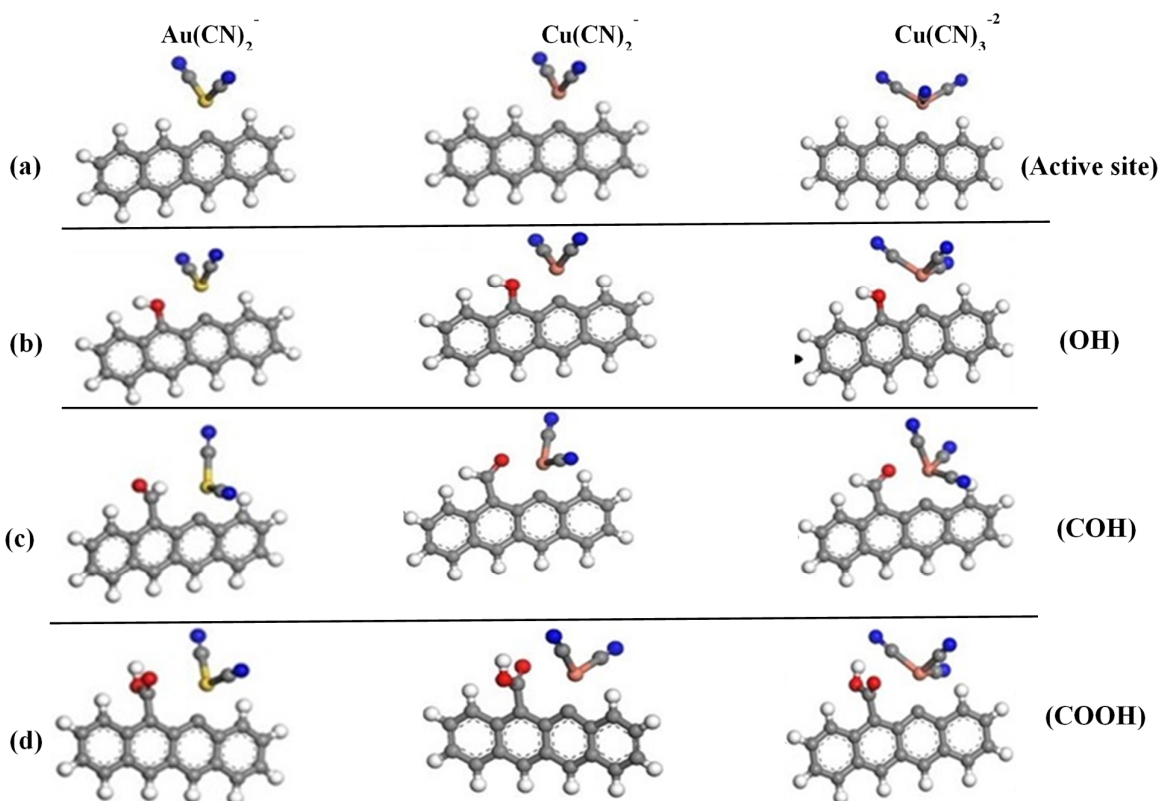

Figure 4. Optimized geometry of interacted copper and gold cyanides on single graphene layer and one unsaturated active site. a) no functional groups, b) OH functional group, c) COH functional group, d) COOH functional group. (yellow: gold, redsphalon: copper, gray: carbon, blue: nitrogen, red: oxygen, and white: hydrogen).

Table 4. Adsorption energy of cyanide complexes of gold and copper with one active site at edge and presence of different functional groups.

Cyanide complex	Adsorption energy (kJ.mole^{-1})			
	No functional group	OH	COH	COOH
$Au(CN)_2^{-1}$	-12.37	-4.80	11.64	-39.07
$Cu(CN)_2^{-1}$	140.21	-25.74	14.88	-53.07
$Cu(CN)_3^{-2}$	57.56	80.85	*	49.88
* Not converged.				

The absorption energy variation in the presence of different functional groups show a very interesting trend. The presence of functional groups has reversed the order of $Au(CN)_2^-$ and $Cu(CN)_2^-$ adsorption trend. In either four or one active sites, gold cyanide shows much higher adsorption comparing to $Cu(CN)_2^-$. However, the presence of OH and COOH functional groups has resulted in much higher adsorption energy for $Cu(CN)_2^-$, while $Au(CN)_2^-$ adsorption has been reduced by OH and increased in COOH surface groups. It can be postulated that OH group has reduced the gold cyanide adsorption by 2.5 times, while has increased the copper dicyanide almost 7 times. On the other hand, the COOH group has improved the absorption of both complexes, while the enhancement for $Cu(CN)_2^-$ is more pronounced. This effect can be attributed to the higher reactivity of copper than gold with oxygen of functional groups as can be clearly observed in the optimized geometries (Figure 4).

It has been reported that the presence of a large amount of oxygenated surface groups such as COOH and OH reduce the gold cyanide absorption [28]. In addition, Souza and his co-workers report that a high amount of surface functional group specifically COOH deteriorate the selectivity of activated carbon for adsorption of gold cyanide, and result in a higher adsorption of $Cu(CN)_2^-$ and lower absorption of $Au(CN)_2^-$ consistent with our modelling data. In their results, the absorption of gold was doubled by increasing the COOH functional groups from 0.3 $\mu eq \cdot m^{-2}$ to 0.8, and about three times for the copper complex.

It can be concluded that the active sites on the graphite edges can play a crucial role in the selectivity of gold adsorption over copper complexes. The unsaturated active sites are preferential sites for adsorption of unpaired anions, while the defect sites on the surface show a minimal tendency for adsorption of both the gold and copper anions. The presence of functional groups can be effective for adsorption enhancement of both unpaired gold and copper cyanide adsorption on the edges. These groups can deteriorate the selectivity of activated carbon for gold cyanide adsorption, and are not suitable for copper bearing gold ores. The COOH functional group among the three investigated groups is the most potent factor for adsorption of $Au(CN)_2^-$ and $Cu(CN)_2^-$ at the edges. In addition, the results of study is in support of the hypothesis for different absorption mechanism and preferential sites of gold and copper complexes on absorbing gold on the carbon surface and absorbing copper on the edges [4].

3.5. Molecular orbital analysis

To further investigate the mechanism of adsorption of unaired gold and copper cyanide complexes on the less active site of surface defects as well as very active sites of graphite edges, the molecular orbital analysis was performed by calculating the frontier orbitals of each specie. For this purpose, the energy levels of the HOMO and LUMO orbitals for the four complexes and the six carbon models used in the previous sections were calculated and demonstrated in Fig. 5. To the direction where electron transfer from cyanide to the activated carbon occurs, or vice versa, the energy difference between HOMO and LUMO of the activated carbon, as well as the energy difference between LUMO of the complex and HOMO of the activated carbon were calculated (Tables 5 and 6). The energy difference between the complex HOMO and the absorbent LUMO is depicted in Table 5, and the difference between the complex LUMO and the adsorbent HOMO is demonstrated in Table 6.
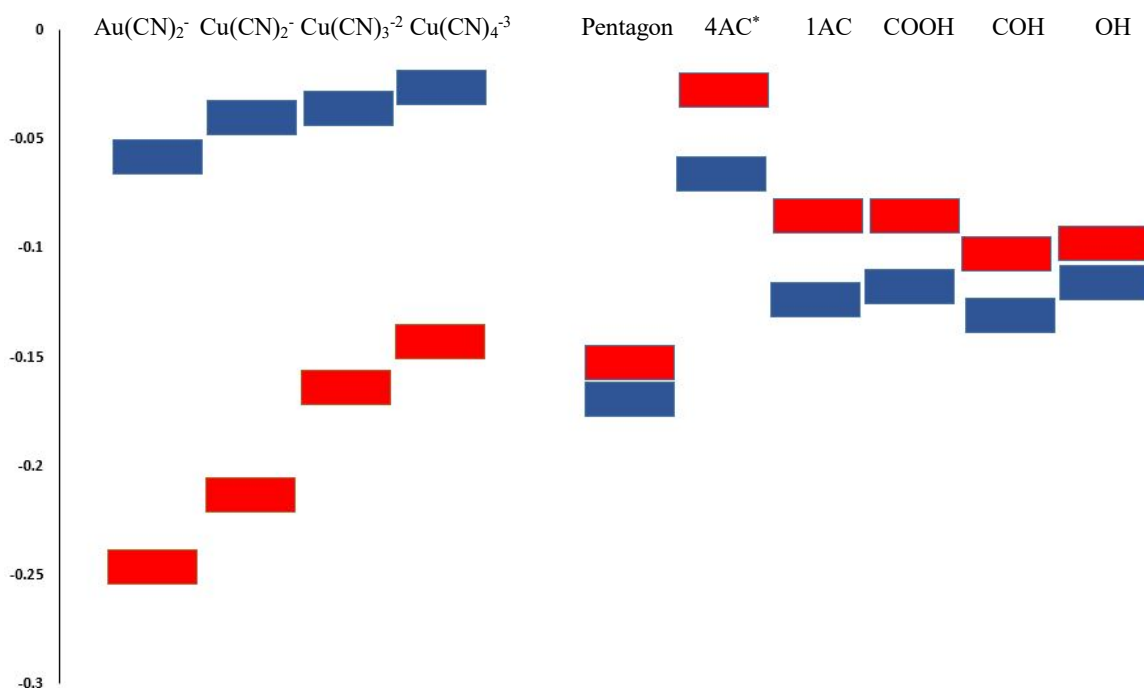
Figure 5. HOMO (red) and LUMO (blue) energy levels for cyanide complexes and carbon models (AC = active site).

Table 5. Difference in energy level between complex LUMO and absorbent HOMO (eV).

Activated Carbon Layers	Cyanide complexes			
	$Au(CN)_2^{-1}$	$Cu(CN)_2^{-1}$	$Cu(CN)_3^{-2}$	$Cu(CN)_4^{-3}$
Concave surface defect	0.107	0.124	0.128	0.137
Edge with 4 active sites	0.009	0.027	0.030	0.040
Edge with 1 active sites	0.066	0.084	0.087	0.097
Edge with 1 active sites & OH group	0.061	0.078	0.082	0.092
Edge with 1 active sites & COH group	0.073	0.090	0.094	0.103
Edge with 1 active sites & CCOH group	0.055	0.072	0.076	0.085

Table 6. Energy difference between complex HOMO and absorbent LUMO (eV).

Activated carbon layers	Cyanide complexes			
	$Au(CN)_2^{-1}$	$Cu(CN)_2^{-1}$	$Cu(CN)_3^{-2}$	$Cu(CN)_4^{-3}$
Concave surface defect	0.086	0.055	0.005	0.015
Edge with 4 active sites	0.022	0. 186	0.136	0.116
Edge with 1 active sites	0.159	0.128	0.077	0.057
Edge with 1 active sites & OH group	0.161	0.130	0.080	0.059
Edge with 1 active sites & COH group	0.142	0.111	0.061	0.041
Edge with 1 active sites & CCOH group	0.144	0.113	0.063	0.042

By comparing the concave pentagon model and the graphene layer with four active sites, the energy difference between the HOMO of the complex and the LUMO of the carbon is lower in concave surface, while for the graphene layer, the difference between the LUMO of the complex and the HOMO of carbon is lower. It shows that absorption of unpaired cyanide anions on the activated carbon surface occurs by electron transfer from the complex to the adsorbent and adsorption onto the activated carbon edges by transferring electrons from the absorbent to the complex. It supports the hypothesis for different adsorption mechanism on the surface and edges of the activated carbon discussed before.

Moreover, based on hard-soft acid-base theory, $Au(CN)_2^-$ is the hardest cyanide complex, and graphene layer with four active sites at the edge is

the hardest absorbent. Since hard-hard interaction is preferable because of the attraction between positive and negative charges [29], adsorption of this complex on the edges is an attraction between the positive charge of gold and the negative charge of carbon.

On the other hand, according to Table 4, the selective absorption on the graphene layer with four active sites follows $Au(CN)_2^{-1} > Cu(CN)_2^{1-} > Cu(CN)_3^{-2} > Cu(CN)_4^{3-}$, which is in accordance with the results of the previous experimental studies and modeling in this study [4] [12].

The saturation of the graphene edges with hydrogen leads to a decrease in the both the HOMO and LUMO energy levels of the graphene layer, so the difference between the energy level of the adsorbent HOMO and complex LUMO amplified consequently. Therefore, a graphene layer with an active site has an inferior ability to share electrons with cyanide complex in comparison with graphene layer with four active sites.

The HOMO-LUMO analysis of functional bearing graphene layers demonstrates that the least negative effect on the adsorption was obtained by the addition of COOH functional groups. The energy level difference between the LUMO of all the complexes and the HOMO of graphene layer for the COOH group is the lowest, which is consistent with the modeling results in this research work and reported experimental data [4]. Also lower selectivity of activated carbon with OH and COOH functional groups for adsorption of gold cyanide over copper cyanides can be clearly observed in the energy level difference between the LUMO of all the complexes and the HOMO of graphene layer. This very well explains the reason for the negative effect of functional groups in selective adsorption of aurocyanide in copper containing gold ores.

4. Conclusions

The role of surface functional groups and preferred adsorption sites in gold and copper cyanide adsorption was investigated using first the principal computational modelling method. The following results were achieved:

- The modelling results propose that the type of defect sites including structural or chemical defect sites of activated carbon play an important role on the adsorption mechanism of gold and copper cyanide complexes.

- The results obtained here in combination with the previously modelling study by Yin and co-workers demonstrates that unpaired cyanide complexes tend to adsorb on the structural defect sites, mostly concave structure, while unpaired gold and copper cyanide anions have the tendency to be adsorbed on unsaturated surface sites.

- The role of oxygen functional groups is promotion of adsorption for both gold and copper cyanide complexes. The elevation of adsorption is more pronounced for copper complexes that can clearly influence the selectivity for gold adsorption by activated carbon.

- The energy levels of the HOMO and LUMO orbitals showed the adsorption of unpaired cyanide anions on the activated carbon surface dominates by electron transfer from the complex to the adsorbent and adsorption onto the activated carbon edges by transferring electrons from the absorbent to the complex.

- Finally, based on the results of this computational modelling study, two different mechanisms can be proposed for adsorption of metal cyanide complexes, the adsorption of paired cyanide complexes on the concave structural defect sites as well as unpaired cyanide complexes on the unsaturated chemical defect sites.

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نقش گروه‌های عاملی در جذب انتخابی سیانید طلا از مس توسط کربن فعال: یک مطالعه DFT

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چکیده:

جذب کمپلکس‌های سیانیدی طلا و مس بر روی کربن فعال با استفاده از نظریه تابع چگالی (DFT) مورد بررسی قرار گرفت. برای معرفی کربن فعال، دو مدل فولرن مانند (نماینده موقعیت‌های نواقص ساختاری) و یک لایه ساده گرافن حاوی گروه‌های عاملی مختلف (نشان‌دهنده موقعیت‌های فعال شیمیایی) مورد استفاده قرار گرفت. موقعیت‌های نواقص ساختاری میزان تمایل به جذب بسیار کمتری را نسبت کمپلکس‌های سیانوری طلا در مقایسه با سایت‌های فعال شیمیایی نشان دادند. میزان انرژی اندرکنش همه کمپلکس‌ها در موقعیت‌های نواقص ساختاری (مقعر) بسیار پایین است. هرچند، لایه گرافن با موقعیت‌های سطحی اشباع نشده بالاترین سطح اندرکنش تقریباً برای همه کمپلکس‌ها به جز $Cu(CN)_4^{3-}$ را نشان داد. اثر گروه‌های عاملی اکسیژن بر روی لبه‌های گرافیت نقش کلیدی را در انتخاب گذیری جذب کمپلکس‌های طلا نسبت به مس نشان داد. این گروه‌ها منجر به افزایش انرژی جذب برای $Cu(CN)_2^-$ در حضور OH و COOH و کاهش انرژی جذب برای $Au(CN)_2^-$ توسط OH و افزایش آن توسط COOH شدند. نتایج این مطالعه نشان دهنده کاهش انتخاب پذیری جذب سیانیدهای طلا نسبت به مس به واسطه محتوای اکسیژن بالاتر کربن فعال هستند. سطوح انرژی اربیتال‌های هومو و لومو نشان می‌دهند که جذب آنیون‌های سیانیدی جفت نشده بر روی سطح کربن فعال از طریق انتقال الکترون از کمپلکس به جاذب و جذب بر روی لبه‌های کربن فعال از طریق انتقال الکترون‌ها از جاذب به کمپلکس اتفاق می‌افتد. نتایج به وضوح نشان می‌دهند که گروه‌های عاملی تمایل به جذب هم کمپلکس‌های سیانیدی طلا (فقط COOH) و هم مس (OH و COOH) را افزایش می‌دهند، هرچند قابلیت جذب انتخابی طلا را نسبت به مس از بین می‌برند.

کلمات کلیدی: سیانید طلا، سیانید مس، کربن فعال، مدلسازی مولکولی، DFT.