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M.Sc. in Industrial Engineering

YASEMİN ŞİRİN

UNIVERSITY OF GAZİANTEP

GRADUATE SCHOOL OF

NATURAL & APPLIED SCIENCES

A COMPUTER-BASED APPROACH FOR MODELING OF REMOVAL OF CD^{2+} ION FROM INDUSTRIAL WASTEWATER WITH POLYACRYLAMIDE COATED RICE HUSK ASH

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Supervisor(s)

Assist. Prof. Dr. Faruk GEYİK

Assist. Prof. Dr. Tuğba TAŞKIN TOK

by

Yasemin ŞİRİN

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Name of the student: Yasemin ŞİRİN

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Approval of the Graduate School of Natural and Applied Sciences

Assoc. Prof. Dr. Metin BEDİR

Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Türkay DERELİ

Head of Department

This is to certify that we have read this thesis and that in our consensus/majority opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science/Doctor of Philosophy.

Assist. Prof. Dr. Tuğba TAŞKIN TOK — Co-Supervisor

Assist. Prof. Dr. Faruk GEYİK — Supervisor

Examining Committee Members	Signature
Assoc. Prof. Dr. Kürşat AĞPAK	…………………..
Assoc. Prof. Dr. Serap ULUSAM SEÇKİNER	………………......
Assist. Prof. Dr. Faruk GEYİK	…………………..
Assist. Prof. Dr. Tuğba TAŞKIN TOK	…………………..
Assist. Prof. Dr. Abdulaziz KAYA	…………………..

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Yasemin ŞİRİN

ABSTRACT

A COMPUTER-BASED APPROACH FOR MODELING OF REMOVAL OF CD^{2+} ION FROM INDUSTRIAL WASTEWATER WITH POLYACRYLAMIDE COATED RICE HUSK ASH

ŞİRİN, Yasemin
M.Sc. in Industrial Engineering
Supervisor: Assist. Prof. Dr. Faruk GEYİK

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Rice makes up %22 of cultivated area and this high production rate makes it an important waste problem. To find a solution to this problem many studies were conducted and a lot of usage area of rice husk emerged. One important usage area of rice husk is using to get rid of heavy metals and textile dyes in the industrial wastewater via adsorption process. The use of rice husks for removal of heavy metal would be a good solution for rice husk storage problems, and it is an economical way for removing heavy metals from industrial wastewater than the other methods.

In this study, a computer-based approach is proposed to optimize binding mechanism of Cd^{2+} ion to polyacrylamide coated rice husk by using geometry optimization and absorption simulation methods. Binding mechanism of Cd^{2+} ion to adsorbent prepared from rice husk explained and modeled by doing the geometry optimizations for determining the most stable structure by Gauss View® 5.0 software.

The adsorption energies of these optimized structures were calculated by using the Material Studio® 6.1 software. Results showed that rice husks can be used as an adsorbent instead of expensive materials such as active carbon. This result indicates that adsorption capacity of rice husk is increasing with polymer treatment. As a conclusion, a computer-based approach was developed by using the obtained results of experimental methods in different studies in literature. It is said that the proposed approach is more quickly and less costly, when compared with experimental methods.

Key words: rice husk, Cd^{2+} ion, geometry optimization, adsorption simulation.

ÖZET

ENDÜSTRİYEL ATIK SULARDAKİ Cd^{2+} İYONUNUN POLİAKRİLAMİD İLE MUAMELE EDİLMİŞ PİRİNÇ KABUĞU KÜLÜ İLE GİDERİMİNİN MODELLENMESİ İÇİN BİLGİSAYAR DESTEKLİ BİR YAKLAŞIM

ŞİRİN, Yasemin
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Pirinç kabuğu dünyadaki ekili tarım alanının yaklaşık %22lik kısmını oluşturmaktadır ve bu yüksek üretim oranı pirinç kabuğunun önemli bir atık problemi olarak ortaya çıkmasına neden olmaktadır. Bu problemi çözmek amacıyla bilim adamları birçok çalışma yapmıştır ve bu çalışmaların sonucunda pirinç kabuğunun birçok uygulama alanı ortaya çıkmıştır. Bu kullanım alanlarının en önemlilerinden biriside pirinç kabuğunun endüstriyel atık sulardaki ağır metal ve tekstil boyarmaddelerin giderimi amacıyla adsorban olarak kullanılmasıdır. Pirinç kabuğunun ağır metal ve tekstil boyarmaddelerin giderimi için kullanılması hem pirinç kabuğunun depolanma problemine bir çözüm sunmaktadır hem de endüstriyel atık suların ağır metallerden temizlenmesinde diğer mevcut yöntemlerden daha ekonomik bir çözüm alternatifidir.

Bu çalışmada Cd^{2+} iyonunun poliakrilamid ile muamele edilmiş pirinç kabuğuna bağlanma mekanizmasını açıklamak için geometri optimizasyonu yöntemi kullanılan bilgisayar destekli bir metot önerilmiştir. Cd^{2+} iyonunun pirinç kabuğundan hazırlanan adsorban yapıya bağlanma mekanizmaları modellenmiş ve bu yapıların geometri optimizasyonları yapılarak en kararlı yapı Gaussian 09 paket programı yardımıyla tespit edilmiştir.

Bir sonraki aşamada optimize edilmiş yapıların adsorpsiyon enerjileri Material Studio 6.1 paket programı kullanılarak hesaplanmıştır. Sonuçlar pirinç kabuğunun aktif karbon gibi pahalı adsorbanların yerine kullanılabileceğini göstermiştir. Sonuç olarak literatürdeki deneysel çalışmalarında sonuçlarından yararlanılarak bilgisayar destekli bir yöntem geliştirilmiştir. Önerdiğimiz yöntemin deneysel yöntemlere göre avantajı daha çabuk bitmesi ve daha az maliyetli olmasıdır.

Anahtar Kelimeler: pirinç kabuğu, Cd^{2+} iyonu, geometri optimizasyonu, adsorpsiyon simülasyonu.

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CHAPTER 1

1. INTRODUCTION

1.1. Introduction

Grain is planted in approximately 700 million hectares of the current cultivated areas in the world, and rice makes up 22% of this area. Also, in production shares, rice comes next after wheat with a share of 28%. If countries were to be compared for rice husk production, China would be first, with India, Indonesia and Bangladesh following. Turkey is among the countries with most increased paddy production within the last decade. The reasons for this increase are the increase in cultivation fields, and the increase in the yield obtained from a unit area. The increase in the cultivation field is due to rice husks being easy to monetize, and that it shows an increase in the profit margin. Table 1.1 shows the rice husk production, the yield, import, export and self-sufficiency data of rice husk in Turkey. As seen in the table, a constant increase in the last ten years is present.

Table 1.1 Values of rice husk of Turkey.

Year	Cultivation (ha)	Production (rice husk) ton	Rice husk yield (ton/ha)	Production (rice) (ton)	Importation (rice) ton	Total supply (rice) ton	Consumption (rice) ton	Exportation (rice) ton
2000	58	350	6.03	210	310.64	516.44	479.51	14.38
2001	59	360	6.1	216	323.27	534.95	501.99	11.76
2002	60	360	6	216	404.72	616.4	572.37	16.04
2003	65	372	5.72	223.2	125.28	344.02	299.95	13.93
2004	70	490	7	294	283.04	571.16	564.64	14.64
2005	85	600	7.06	360	221.25	577.65	534.99	16.58
2006	99.1	696	7.02	417.6	167.98	581.4	555.32	16.79
2007	93.9	648	6.9	388.8	236.364	621.27	612.87	20.94
2008	99.49	753	7.57	451.995	183.62	631.09	556.99	36.49
2009	96.75	750	7.75	450	336.2	781.69	702.51	40.46
2010	99	860	8.69	516	371	0	600	52

According to TUIK data in 2010 rice production is 860 thousand tons, in 2011, 900 thousand tons with an increase of % 4.7 and in 2012 it is 860 thousand tons with a reduction of % 2.2. In our country, the annual consumption of rice is about 600 thousand tons.

Table 1.2 shows the rice production value of major countries in rice production since 2000. As it seen in the table there is a general increases in the rice production in the world and China and India are the most rice-producing countries.

Table 1.2 Rice Production Values of Major Countries since the Year 2000.

COUNTRIES	2000/ 01	2001/ 02	2002/ 03	2003/ 04	2004/ 05	2005/ 06	2006/ 07	2007/ 08	2008/ 09	2009/ 10
China	131.5	124.3	122.2	112.5	125.4	126.4	127.2	130.2	134.3	137
India	85	93.3	71.8	88.5	83.1	91.8	93.4	96.7	99.2	89.1
Indonesia	33	33	33.4	35	34.8	35	35.3	37	38.3	36.4
Bangladesh	25.1	24.3	25.2	26.2	25.6	28.8	29	28.8	31	31
Vietnam	20.5	21	21.5	22.1	22.7	22.8	22.9	24.4	24.4	25
Thailand	17.1	17.5	17.2	18	17.4	18.2	18.3	19.8	19.9	20.3
Philippines	8.1	8.5	8.5	9.2	9.4	9.8	9.8	10.5	10.8	9.8
Turkey	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.4	0.4	0.4
Others	79	78.2	79	80.9	83.1	85.5	84.6	86.7	88.8	91.9
World	399.5	400.3	379	392.6	401.8	418.6	420.8	433.6	448.1	440.9

Source: United States Department of Agriculture (USDA) (November 2011)

According to USDA November,2013 reports ; amount of total world rice production in 2011 / 2012 years 465.81 million metric tons, and 2012/2013 estimation is 468.96 million metric tons.

As 22% of the produced rice is husks, and the remaining is rice and bran, the high production in the world and in Turkey makes the rice husk an important waste problem. Many studies were conducted by scientists to make use of this husk, and as a result of these studies, it was found that rice husk can be used in various areas, from construction to solar panel production. In this study, using rice husks to get rid of heavy metals and textile dye pollution from industrial wastewaters will be covered.

Due to the increase in necessities for limited water resources and their misuse, legislations in order to protect the environment have become a requirement in the world and in Turkey. The lower limits for heavy metal concentrations in industrial wastewater have been determined by legislations and WHO, as they may contain high amounts of toxic compounds and pollutants. While these toxic compounds have different effects and components for each industry, heavy metals are the most common of these components (Hall et al., 1966). The heavy metals, which are harmful even in trace amounts, can be listed as: Cu, Cd, Cr, Pb, Mn, Hg, Zn (Kocataş, 2002).

The water pollution occurs after needs are met, such as industrial uses and agricultural irrigation. After being polluted, they are released to the environment and therefore cannot be reused. Nowadays, less than 3% of water can be used as drinkable water. For this reason, precautions must be taken before polluted water is released into the environment, so industrial wastewater, hospital and quarantine wastewater should not be directly release into the sewage system (Koçyiğit, 1999).

1.2. Aim of the study

This study aims a computer-based approach to optimize binding mechanism of rice husk by using geometry optimization and absorption simulation methods. By this aim, the rice husk's adsorption mechanism of Cd^{2+} which is found in industrial wastewater will be examined. A computer-based approach will be developed by using the obtained results of experimental methods in different studies in literature. Thus, it is proposed an efficient optimization method that is more quickly and less costly, when compared with experimental methods.

1.3. Outline of the study

In the first part of the study, the importance of the heavy metals in industrial wastewater and finding an economical solution to, its harmful effect to biological systems and human health are mentioned. The chemical and physical properties of rice husks and their usage area are covered.

In the second part, the binding mechanism of Cd^{2+} ion to rice husk was attempted to be explained via molecular mechanical methods. The probable ways of Cd^{2+} binding to the rice husk was modeled and by doing the geometry optimizations, the most stable structure was determined. All of the optimization techniques that were used are explained. In this section, Gaussian 09 package program was used.

In the third part, the adsorption properties of the possible structures were examined by using the Material Studio 6.1 package program. The theories behind these modeling's were explained in detail. As a result, the adsorption energies that are calculated by the program are assessed.

In the last part of the study we gave computational results of geometry optimization and adsorption simulation. We discussed results of these processes and gave a general conclusion of our study. It was seen that rice husks can replace expensive adsorbents- such as active carbon- by means of simulation.

CHAPTER 2

2. LITERATURE REVIEW and BACKGROUND

2.1. General Information about Heavy Metals

Metals which have specific gravity more than 5, or in other words, metals whose atomic number is greater than 20 (such as Ag, As, Cd, Fe....) are called heavy metals. There are more than 60 metals in this group (Pourshakiba, 2012). Among them Cd, Ni, Cu, Pb, Zn, Hg, Co, As and Cr tend to accumulate in the natural environment and they are toxic elements (Pourshakiba, 2012).

Metals are the oldest toxins known to man, and depending on their concentration, can be harmful to live systems. Nowadays, the increase in heavy metal pollution is caused by mining activities, using fossil fuels, the rapid increase in industrialization, the release of metal containing wastes to the environment, etc. (El- Sokkary et al., 2005). The reason that heavy metals are in the toxic group is because they are not biodegradable and cannot be broken down into harmless compounds (Athar and Vohora, 1995). Cadmium is among the most toxic heavy metals (Katalay and Parlak, 2004). The reason that this metal is in the scope of this study is its vast usage area and its high content in cigarettes (Satoh et al., 2002).

Since the harmful effects of heavy metals have been noticed and their areas of use have increased, studies regarding this topic have increased. When the spreading of the heavy metals is studied, it was observed that heavy metal pollution is caused more by industrial activities of people than natural reasons (Alexander, 2002).

The heavy metals in industrial wastewater make water resources impossible to be used as drinking water for crop irrigation. The sources that are the biggest causes of heavy metal pollution can be listed as: coal and other mining industries, steel and other metal industries, automotive factories, cement production, thermal power plants, glass production, incinerators, industries such as electronics and paint, batteries, catalytic, medical wastes (Lanouette and Paulson, 1976). The following table provides information about the metal kinds released to the environment from the basic industries:

Table 2.1 Distribution of heavy metals in industrial wastes (Öztekin, 2009).

Industry	Cd	Cr	Cu	Hg	Pb	Ni	Sn	Zn	Fe	Mn
Paper Industry	-	+	+	+	+	+	+	+	-	-
Petrochemistry	+	+	-	+	+	-	+	+	+	-
Chlor-alkali Production	+	+	-	+	+	-	+	+	+	-
Fertilizer Industry	+	+	+	+	+	+	+	+	+	+
Iron-Steel Industry	+	+	+	+	+	+	+	+	+	-
Energy Production (thermal)	+	+	+	+	+	+	+	+	-	-
Metal Industry	+	+	+	+	+	-	+	+	-	-
Coating Industry	+	+	+	+	-	+	-	-	-	-
Glass, cement production	-	+	-	-	-	-	-	-	-	-
Textile Industry	-	+	-	-	-	-	-	-	-	-
Leather Industry	-	+	-	-	-	-	-	-	-	-

According to table 2.1, Cd^{2+} ion released to the environment from petrochemical plants, chlorine-alkali production, fertilizer industry, iron-steel industry, energy production, metal industry, coating industry.

Some of the heavy metals (copper, for example) partake in biological reactions in live systems, so they should be taken by nutrients. They are called vital metals. However, the presence of some non-vital metals (mercury, for example) is very dangerous for living beings (Doyurum, 2005; Duffus and Wotrh, 1996).

If the rate the heavy metals enter the human body via water, food and other ways is more than the rate of their purge, this causes an accumulation in the body. In order to control this, the amount of heavy metal in food and drinking water and their levels must be carefully monitored by legal organizations.

Due to these negative effects, wastewater that contains heavy metal must be filtered, and adsorption, ion exchange, chemical sedimentation and reverse osmosis are among the methods used for filtering. However, these units are far from being economical and practical in terms of facilities, equipment and other aspects. For this reason, using bio wastes, such as rice husks, as adsorbents in order to get rid of the heavy metals in wastewater was focused on (Pourshakiba, 2012).

The table below shows the higher limit of heavy metal concentration values in drinking water and in aquatic habitat allowed by WHO, EU, USA, Russia and TSE 226.

Table 2.2. Acceptable maximum concentrations of heavy metals (Aksoy, 2005).

Heavy Metal Usage (mg /L)	DRINKING WATER				
	WHO	EU	USA	RUSYA	TSE-226
Cadmium	0.003	0.005	0.005	0.003	0.0005
Chrome	0.05	0.05	0.1	0.05	0.05
Cobalt	-	-	-	0.1	-
Copper	2	0.1-3.0	1	2	1.5
Iron	0.3	0.2	0.3	0.3	1
Lead	0.01	0.05	0.015	0.01	0.05
Manganese	0.5	0.05	0.05	0.5	0.5
Nickel	0.02	0.05	-	0.02	-
Zinc	3	0.1-5.0	5	5	15

2.2. General Information About Cd^{2+} Ion

Cadmium is in the 2B group in the periodic table; it is white and is of medium hardness. Cadmium is not found pure in nature, it is found as cadmium oxide, cadmium chloride, cadmium sulfate and sulfide compounds (Méndez-Armenta and Ríos, 2007). It is obtained during zinc production, by electrolysis, during melting copper and lead, and from lithopone wastes (Ün, 1968). The general properties of cadmium are tabulated below:

Table 2.3 General properties of cadmium ion (Ün, 1968).

SYMBOL	Cd
DISCOVERED BY	Fredrich Stromeyer in 1817
ATOMIC NUMBER	48
ATOMIC MASS	112.41
MELTING POINT, ^{0}C	320.9
BOILING POINT, ^{0}C	767.3
DENSITY g/cm3	8,65
IONISATION ENERGY (kcal/mol)	207

Basic industrial usage areas are; (Murugavel et al., 2007; Kirkham, 2006)

- Plating and electroplating industry
- as a neutron absorber in nuclear power plants
- aircraft and shipbuilding industries
- in plastic production
- Paint and nickel- cadmium battery industry
- For purification of zinc, copper and lead ores
- In glass and ceramic industry
- Apart from these areas it can be found in phosphate-based fertilizers, detergents and are refined petroleum products.

As a result of wide usage areas, cadmium pollution results as an important problem. Exposure to cadmium is commonly seen in highly industrialized or mining areas. According to EU standards, the density of cadmium in normal air is 0.005 µg / m^3, while this amount is much higher in regions surrounding battery factories (Tezcan, 2011).

Cadmium is a heavy metal with known negative effects and toxic properties. The toxic property of cadmium comes from switching places with metal ions such as Zn^{+2}, Cu^{+2} and Ca^{+2} in metalloenzymes, and the affinity to bind with thiol(-SH) containing biostructures such as proteins and enzymes (Brzóska and Moniuszko-Jakoniuk, 2001).

As cadmium is released in the released wastes, it pollutes the water and soil. The cadmium accumulated in the soil and water reaches humans and animals indirectly by food and drinking water. Cadmium generally enters the human body by ingestion or inhalation. One of the most important ways of inhaling cadmium is by cigarettes, and there is 1-2 µg of cadmium in a cigarette (Aydogdu et al., 2007). Although this amount appears to be small, due to repetition, it reaches a harmful amount. Contact with skin is not effective enough for it to be toxic.

According to the World Health Organization's (WHO) classification, cadmium is a grade 1 carcinogen, and is harmful even in small concentration (Duffus, 1980). Cadmium is most abundant in the soil, and humans take it in their systems mostly by food. Such foods are: specialty meats like liver and kidneys, plants and shelled seafood, seafood such as mussels and seaweed (Ho et al., 2002). Cadmium in the soil is transferred by the food chain from plants to animals and humans. While there is no cadmium in a newborn baby, the amount of cadmium in the body increases with age and the amount can go up to 40 mg in a normally healthy person (Doyurum, 2005).

Another reason that humans are exposed to cadmium is the used of cadmium containing pesticides, phosphate fertilizers and fertilizers contaminated by commercial wastes for agriculture.

If the harmful effects of cadmium to human health and related sicknesses are to be summarized (Doyurum, 2005; Duffus and Wotrh, 1996).

1. Cadmium builds up in kidneys and damages the filtering mechanism. An overdose of cadmium (60-480 μg/ g kidney) causes a destructive effect on kidneys. It will cause the required proteins and glucose to be purged from the body, resulting in kidney disorders.

2. It causes acute poisoning. The initial symptoms are malaise, headaches, fever, perspiration, tension in muscles, aches are accompanies with vomiting, and if there are no more exposure, the symptoms disappear within a week.

3. The most important disorders that are a result of chronic cadmium poisoning are lung and prostate cancers.

4. Cadmium disrupts the calcium phosphate and vitamin D mechanisms, causing osteoporosis and related disorders.

5. It also causes anemia, teeth loss, and loss of the olfactory sense.

6. Other harmful effects can be listed as shortness in breath, back and leg aches, and joint pains.

7. Studies also show that cadmium has a negative effect on the reproductive and endocrine system.

8. Another study showed in highly polluted areas or in industries that use cadmium heavily, the incidence of hypertension and heart diseases increase.

2.3. Usage Areas of Rice Husk

Rice husk is an agricultural waste which can be found in abundance in nature. It has a wide range of usage area from construction industry to energy sector because of high silica ratio of its structure and its heat insulation feature. We will give brief information about this usage areas and recent studies in these areas.

2.3.1. Usage In The Construction Industry

Considering that it will be useful for protection of energy sources and it will be an alternative solution for an important waste problem there had been made several studies about the usage of rice husk in construction industry. If rice husk is burned to a certain temperature (400-600 °C) in a controlled manner we can obtain a high pozzolanic featured ash.

Görhan and Şimşek (2013) made an investigation about how rice husk addition affects the porosity and the thermal conductivity of clay bricks .They observed that with rice husk addition porosity and water absorption has been increasing and thermal conductivity coefficient decreasing.

Yuzer et al. (2013) has studied the influence of rice husk addition to concrete and concluded that rice husk addition modifies and makes improvement physical and thermo physical properties (such as density, thermal conductivity, ultrasonic pulse velocity) of concrete but however leads a small decreasing in compressive strength. As an important result of this study, rice husk can be used instead of polypropylene fibers because of reducing vapor pressure and thus prevents spalling and it can adsorb harmful gases which occur at production.

Hamzeh et al. (2013) investigated the effect of rice husk and fibrous materials addition on fiber-cement composites and they showed that mechanical and physical properties were affected by the addition of rice husk ash. Water absorption and bulk density of the cement significantly reduced.

2.3.2. Usage for Energy Purposes

Recently, there is a worldwide intensive research about the use of biomass as an alternative source of energy instead of the detrimental sources such as fossil fuels. As a source of biomass, rice husk has already been used for energy purposes in various areas. Some of them are cook stoves, process heat generation for rice drying, as fuel for boilers which generate heat for steam engines (gasification), and most common is for generating electricity. Due to its high calorific value, 3410 rice husk is a preferable energy source.

Figure 2.1 Modern power plant of rice husk.

2.3.3. Usage for Production of refractory materials -ceramics- glasses

Because of its heat absorption capability rice husk can be used in refractory material production and can be used as an insulating material (Yıldız et al., 2007). Beside of these it can be used as a raw material for ceramic production (Berkin, 2006).

Rice husk can be used in colorless and color production when sintered at 1000 °C. Color is depend on the chemicals doped, i.e., when CuO doped light blue color , MnO_2 doped brown, if CoO doped deep blue, Er_2O_3 doped pink , and if Cr_2O_3 doped green color can be obtained (Kaewkhao and Limsuwan, 2012).

Andreola et al. (2013) and friends directed a study which is about the production of glass-ceramic by using rice husk ash (RHA) as silica source and the results approve that rice husk ash can be used as a silica sources for the production of nepheline – fosterite glass ceramics. There are some benefits of using rice husk ash instead of silica such as; an alternative solution for landfill problem of a biomass residue and minimization of the natural raw material consumption.

2.3.4. Usage for Chemical Production

Silica is most important inorganic component of rice husk and because of that there is an intensive study about developing a productive and efficient process of producing amorphous silica from rice husk. Carmona et al. (2013) produced amorphous silica using soft acid solutions and have found micro and nano structure silica particles.

Zulkifli et al. (2013) produced structurally controlled non- crystalline silica particles from rice husk and the produced silica is appropriate for use as filler in dental restoration composites.

Zeolite (ZSM-5) particles can be synthesized from silica which is extracted from rice husk ash in hydrothermal condition at 150 °C/72–96 h. (Dey et al., 2013).

Different kinds of catalyst can be prepared from rice husk ash because of its silica content. For example, Li_2SiO_3 highly active catalyst was prepared from rice husk ash silica for biodiesel production (Chen et al., 2013) .

Mesoporous activated carbon can be prepared from rice husk ash. Since active carbon is highly adsorbent, it is used in the industry as decolorant and deodorant.

Due to its silica content rice husk have become a raw material for the production of some silicon-based materials such as , silica gel, films silicate, sodium silicate, silicon carbide, silicon nitride, silicon tetrachloride, pure silicon (Sadıç, 2008).

Apart from these areas it can be used as a wiper for flooring and also we can make use of the abrasive nature of the ash for clearing and polishing of the metal surfaces (Berkin, 2006).

Alkali treated rice husk is often used to feed the animals because of its protein and energy content.

2.3.5. Usage as an Adsorbent

Besides industrialization have many benefits also it has some unwanted effects to environment such as the release of the heavy metals into the environment and this problem have created a great concern in the all over the world. One important reason of this global interest is persistence and toxicity of this heavy metal such as Zn, Pb, Ni and Cd. These toxic metals contaminate water via waste water from different industries such as mining, pigments, alloys, dezincification, textile industry and other industrial wastes (Tiwari et al., 1989). Effective and safe purification of industrial wastewater is very important and for being an alternative solution usage of agricultural and low cost products and sorbents has been widely investigated. Recent studies mostly based on agricultural products and their derivatives such as saw dust, treated and untreated orange waste, treated and untreated rice husk and etc. (Taty-Costodes et al., 2003; Sharma and Kareer, 2006; Sharma et al., 2006; Kumar and Bandyopadhyay, 2006; Ghimire et al., 2008).

In this section we gave short information about adsorbent features of an agricultural waste rice husk and studies about this topic. According to literature we can say that chemical modifications positively affect the adsorption capacity of these agricultural sorbents.

2.3.5.1. Cr (VI)

Sugashini et al. (2013) investigated adsorbent feature of the ozone treated carbonized rice husk (OTRHC) for the removal of Cr (VI) ions in continuous process and with %81.6 adsorption of Cr (VI), total adsorption capacity of OTRHC was found higher when compared to other adsorbents.

Oladja et al. (2013) compared adsorption capacity of iron (Fe) coated rice husk derived silica and raw rice husk silica. The predicted sorption capacity (mg/g) of the iron coated rice husk silica (63.69) was higher than that of the row rice husk silica (61.35). The value of the mean free energy (kJ/mol) of sorption of iron coated (267.26) and raw (100.00) rice husk silica , and the differences in the peak positions of some functional groups on the Cr(VI) sorbents showed chemisorption as mechanism of Cr(VI).

2.3.5.2. As (V)

Arsenic is a great danger for drinking water and like all over the world in Turkey according to Human Consumption Purposeful Water Regulations which is published by Ministry of Health in 2008, limit of arsenic concentration is determined as 10 μg/L for drinking water.

Various treatment methods have been tried for the removal of arsenic from waste water such as, reverse osmosis and nano-filtration, co-precipitation, coagulation-microfiltration but because of it is effective and cheap method then others, adsorption gathered more interest (Leupin and Hug, 2005; Han et al., 2002; Urase et al., 1998).

Pehlivan et al. (2013) modified rice husk with iron oxyhydroxide (RH-FeOOH) and they showed that modified rice husk is suitable and low cost adsorbent for removing As(V) from impure water with the sorption capacity of (RH-FeOOH) 2.5 mg/g.

2.3.5.3. Nitrate

Katal et al. (2013) and friends prepared anionic rice husk and investigated adsorption properties for nitrate removal. The optimum conditions were found to be: a sorbent dose of 0.4 g /100 mL, contact time of 90 min, and in this conditions removal efficiency was 94.3% for the NO_3^-. So this absorbent can be used and has a high efficient for the removal of NO_3^- from urban water.

2.3.5.4. Cu(II)

Activated carbons from rice husk was prepared and adsorption of Cu(II) has studied by Zhang and friends and they found that the optimum conditions for Cu(II) adsorption on the rice husk derived carbons was an equilibrium time of 24 h and pH value of 5.0. (Zhang et al., 2011).

2.3.5.5. Hg(II)

Rice husk coated with polyaniline nanocomposite was prepared for removal of Hg(II) from aqua solution by Ghorbani and friends. They found optimum conditions pH 9, adsorbent dosage of 10 g/L. and 20 min of contact time for mercury removal. As a result of this study adsorption efficiency of polyaniline / rice husk nanocomposites was found to be higher than raw rice husk ash and polyaniline (Ghorbani et al., 2011).

2.3.5.6. Fluoride

WHO limits the fluoride content of water with the 0.5-1.5 mg/L, because surplus of fluoride causes dental and skeletal flourosis. Because of its importance several techniques for removal of fluoride have been studied and according to Ganvir and

Das (2011) cheapest, simple and environmentally friendly method is based on coating rice husk ash (RHA) with aluminum hydroxide. RHA is an easy available and cheap raw material. The results of this study showed that aluminum hydroxide coated RHA have perfect fluoride removal efficiency with the adsorption capacity of between 9 - 10 mg/g.

2.3.5.7. Cr (III)

Kanwal et al. (2012) studied the adsorption of Cr (III) from water by polyaniline composites with rice husk and saw dust and they determined the optimum conditions for absorption of Cr (III). According to this study adsorption of Cr (III) on these composites occurs spontaneously (Kanwal et al., 2012).

2.3.5.8. Humic acid

Imyim and Prapalimrungsi (2010) made a study which compares raw rice husk ash and aminopropyl functionalized rice husk in terms of adsorption capacity of humic acid from water. The adsorption capacity of functionalized rice husk was higher than that of RHA and maximum adsorption capacity was 8.2 mg/g. at pH 6. As a result aminopropyl functionalized rice husk found suitable for humic acid removal.

2.3.5.9. Zn^{2+}

Zn is one of the toxic heavy metal and the World Health Organization standard of Zn ion concentration in drinking water is 2.00 ppm. Sharma et al. (2012) searched Zn^{+2} adsorption capacity of treated rice husk. Optimum conditions were found like this, pH 8, 3 hour contact time and concentration range 30 to 300 mgL^{-1} and in these conditions maximum adsorption was found 86.6%. The result of this study showed that treated rice husk can be used as an efficient adsorbent for the removal of Zn^{+2} from aqueous solutions.

Ghorbani and Eisazadeh (2012) researched adsorption properties of polypyrrole (PPy) and polyaniline (PAn) coated on rice husk ash (RHA) composites. They compared adsorption capacity of polyaniline, polypyrrole and their blends and nanocomposites with rice husk ash. As a result PPy/RHA and PAn/RHA nanocomposites can be used as an efficient adsorbent an there isn't a big difference between them for removal of anions, heavy metals, color and COD from textile wastewater.

2.3.5.10.Textile Dyes

Lin and friends prepared activated carbons from treated rice husk and then they analyzed methylene blue adsorption performance of this absorbent. Optimum adsorption conditions were determined and the results showed that activated carbons prepared from NaOH pretreated rice husk have a perfect adsorption capacity of methylene blue molecules (Lin et al., 2013).

Adsorptive removal of Eriochrome Black T (EBT) from aqueous solution with the aid of activated carbon prepared from rice husk was studied by Luna and friends. In this adsorption study they showed that there is a positive correlation between the initial dye concentration, adsorbent dose, pH and removal percentage of EBT. As a result of this study they said that in the optimum conditions, 95 ppm initial dye concentration, 2.0 g adsorbent dose and pH 2, maximum %96 EBT removal occurs (Luna et al., 2013).

Chakraborty et al. (2011) has studied Crystal Violet (CV) adsorption onto NaOH-modified rice husk (NMRH). Experiments were carried out in various contact time, pH range (2–10), adsorbent dose (0.5–5 g) and temperature (293, 303 and 313 K) and results showed that the adsorption is spontaneous and exothermic.

Safa and Bhatti (2011) described the biosorption of rice husk for the adsorptive removal of Direct Red-31 and Direct Orange-26 textile dyes from aqueous solutions. A 5^3 factorial design experiment was used to optimize the process parameters for adsorption of this textile dyes. Three factors are biosorbent dose, initial dye concentration, and pH at five levels. Analysis of variance (ANOVA), *F*-test and *p*-values were used to study for explaining interaction effects and a good regression coefficient (0.999) was found. A maximum removal capacity of Direct Red-31 and Direct Orange-26 are; 57.88 and 36.14 mg/g were found.

Chowdhury et al. (2011) tested rice husk treated with NaOH as a low cost adsorbent for the removal of malachite green from aqueous solution. Among the parameters of adsorption experiments (pH, initial dye concentration, contact time and temperature) it was found that adsorption capacity is extremely dependent on pH of the medium. Studies showed that the adsorption of malachite green by NaOH- treated rice husk is spontaneous and endothermic nature.

Lakshmi et al. (2009) and friends studied adsorption of Indigo Carmine (IC) dye by using rice husk ash (RHA). The optimum conditions of adsorption determined as $pH_0 = 5.4$, $t = 8$ h and $m = 10.0$ g/l and it s observed that there is correlation between temperature and rice husk ash adsorption of IC dye. Thermochemical values showed practicable and spontaneous adsorption of Indigo Carmine ye on to rice husk ash.

In this section we gave some examples from literature about studies on adsorption activity of different treated rice husk for adsorption of different textile dyes from waste water of industrial organizations. And this all studies showed that rice husk is low cost and environmentally friendly adsorbent for dye removing from waste water.

2.3.5.11. Cd (II)

Cd is one of the major toxic metals which are danger for human health. World Health Organization limits the ratio of Cd ions in drinking water to 0.005 ppm. Because of that studies have been conducted about effective removal of Cd from industrial waste water. Some of them are;

Srivastava et al. (2009) reported the competitive adsorptive removal of cadmium (Cd(II)) and zinc (Zn(II)) ions by rice husk ash (RHA). Studies showed that adsorption capacity of RHA is affected from the initial concentration and pH_0. In this experiment adsorption of Cd(II) ion is less than that of Zn(II) ion, and this result is compatible to the unique Cd and Zn adsorption data.

Kumar and Bandyopadhyay (2006) investigated the sorption of Cd(II) from aqueous solution by an agricultural waste, rice husk. In this study Cd(II) removal efficiency of raw rice husk (RRH) , epichlorohydrin treated rice husk (ERH), NaOH treated rice husk (NRH), and sodium bicarbonate treated rice husk (NCRH) were examined. The most efficient , cheap and rapid removal of Cd(II) was found to be by NCRH and because of this result NCRH could be a perfect alternative for removal of metallic ions from waste water.

Srivastava et al. (2009) studied about competitive adsorption of cadmium (Cd (II)) and nickel (Ni(II)) ions from aqueous solution onto rice husk ash (RHA). In this binary system adsorption capacities for the Ni(II) was found to be more then Cd(II) ions and the combined equilibrium sorption of Cd(II) and Ni(II) ions onto rice husk ash is found to be antagonistic (Srivastava et al., 2009).

Ye et al. (2010) tested natural and modified rice husk in terms of removal efficiency of Cd (II) ions from water. According to the results the Cd(II) adsorption capacity was 73.96 and the adsorption capacity of alkali treated rice husk was 125.94 mg/g. They showed that modified rice husk had faster higher adsorption capacities than the natural rice husk. The Cd(II) adsorptions on the two adsorbents have positive correlation with and the optimum pH for Cd(II) adsorption is 6.5. This study also showed that desorbability of Cd (II) is very high (95.8–99.1%).

Sharma et al. (2009) conducted a study about the removal of cadmium ions by rice husk and saw dust with acryl amide. They found optimum removal conditions was found to be at pH 9 and contact time of 180 min , 30-300 mg L^{-1} and in this conditions maximum removal of 85% Cd^{2+} observed for both the adsorbents. According to this study desorption can be made by the help of 0.5M HCl and the recovery of the metal was 98% in the first cycle and is reduced to 90% in the third cycle. The results showed that polyacrylamide grafted rice husk/saw dust are efficient and cost effective adsorbents for cadmium ion removal and if grafted rice husk compared with activated carbon rice husk although their adsorption capacity are almost same for Cd^{2+} removal, rice husk is more economical then other activated carbon.

2.4. Adsorption

One of the most important methods in removing harmful chemicals from wastewater is adsorption. Adsorption occurs when an ion or molecule holds on to a surface due to attraction forces, and this happens from unequivalent forces. The act of the bound ions leaving the surface is called desorption (Sarıkaya, 1997). In adsorption process; one of the two components is called adsorbate, and the matter which is adhering on the solid surface is called as adsorbed, and the adsorbed chemical (adsorbate) can be more than one. Sorbent, sorbate and sorbtive terms and the sorption terms are used for simultaneous adsorption and desorption (Karagöz, 2011).

Adsorption occurs by itself under constant temperature and pressure. When the thermodynamic parameters are considered, the free energy of adsorption is negative as is happens on its own, the ions bind to a solid surface and they become more stable so the entropy of adsorption is negative, and due to the thermodynamic equality, the enthalpy of adsorption is negative. The fact that the adsorption enthalpy is negative, this shows that adsorption is an exothermic process (Pourshakiba, 2012).

The main factors affecting the efficiency of adsorption are, the physical and chemical properties of adsorbent, interaction degree between adsorbent and the adsorbed material and the characteristics of the adsorption environment. These parameters can be summarized in such subtitles; (Sarısoy, 2002).

- Surface area and surface features of adsorbent
- Pore characteristics of adsorbent
- Amount of adsorbent
- Solubility and concentration
- The temperature of medium
- pH value of medium
- Adsorption time
- Other ions in adsorption medium.

Based on the attraction forces between the molecules in the solution and the adsorbed surface, there are four types of adsorption, with physical and chemical adsorption being the most important ones. The other two are biological and ionic adsorption (Sarıkaya, 1993).

Physical adsorption is generally occurred in medium where equilibrium is easily obtained and by intermolecular forces. For this reason it is commonly dubbed as “Van der Waals Adsorption”. Chemical adsorption occurs by electron sharing or by electron transfer and it requires chemical bonding. In ionic adsorption, the ionic strength on the adsorbent and the adsorbate is important. While the mechanism of biological adsorption is not fully explained, it occurs by transferring microorganisms on inert material (Sarıkaya, 1993).

Table 3.3 below summarizes the differences between physical and chemical adsorption (Thomas and Thomas, 1997).

Table 2.4. Differences between physical and chemical adsorption

PHYSICAL ADSORPTION	CHEMICAL ADSORPTION
Adsorption doesn't require sharing or transfer of electrons and so interacting species protect their structure.	Chemical adsorption requires chemical bonding and it doesn't occur between all binary.
Interactions are all reversible and in the same temperature desorption can occur.	It is irreversible.
It is not location specific, the adsorbed molecules can cover the entire surface.	It is location specific.
Heat of adsorption is generally low and upper limit is 20 kcal/mol.	Heat of the chemical adsorption can be more than 200 kcal/mol
The adsorbed layer is thicker than one molecule (multi-layered).	It occurs in a single layer.
It is a general phenomenon which has a low selectivity.	It depends on the reactivity of the adsorbent and adsorbate.
Adsorbed molecule protects itself and it can return to its original form and liquid phase with desorption.	Structure of the chemically adsorbed molecule changes and can be recovered with desorption.
Generally it reaches the equilibrium quickly.	Activation energy is needed and it reaches the equilibrium slowly.
Occurs in low temperatures and decreases when temperature rises.	Occurs in high temperatures and it increases when temperature increases.
Van der waals forces are active.	Chemical bonding forces are active.

CHAPTER 3

3. MATERIAL and METHODS

3.1. Proposed Method for Adsorption Simulation

In molecular simulation, optimization or minimization is the most common application which applied to the system being examined. Sketching generally generates molecules which has high energy configuration and because of that we need to optimize a structure after it has been sketched.

The molecular projection of the rice husk, polyacrylamide, and the combined structure are shown in computer media, with their molecular optimizations. After that, the probable structures that will occur after Cd^{2+} is adsorbed in the medium are drawn and optimized on computer. The optimization energies are compared, and the structure with the lowest energy is determined as the most stable structure; it was also determined that Cd^{2+} binds to the adsorbent from that part. All of these studies were done by using Gaussian 09 package software.

After optimization we use a computer program, Material Studio 6.1, for examining the adsorption property of polymer coated rice husk. We calculated the adsorption energies of our possible 36 structure an unmodified rice husk with aid of Adsorption Locater of this program. Afterwards, the adsorption energies in which the Cd^{2+} ion binds in single, double, quadruple and sextant bonds and finally the structure with the highest adsorption energy was determined.

In Figure 3.1, we illustrate general algorithm of adsorption simulation that we used in our study.

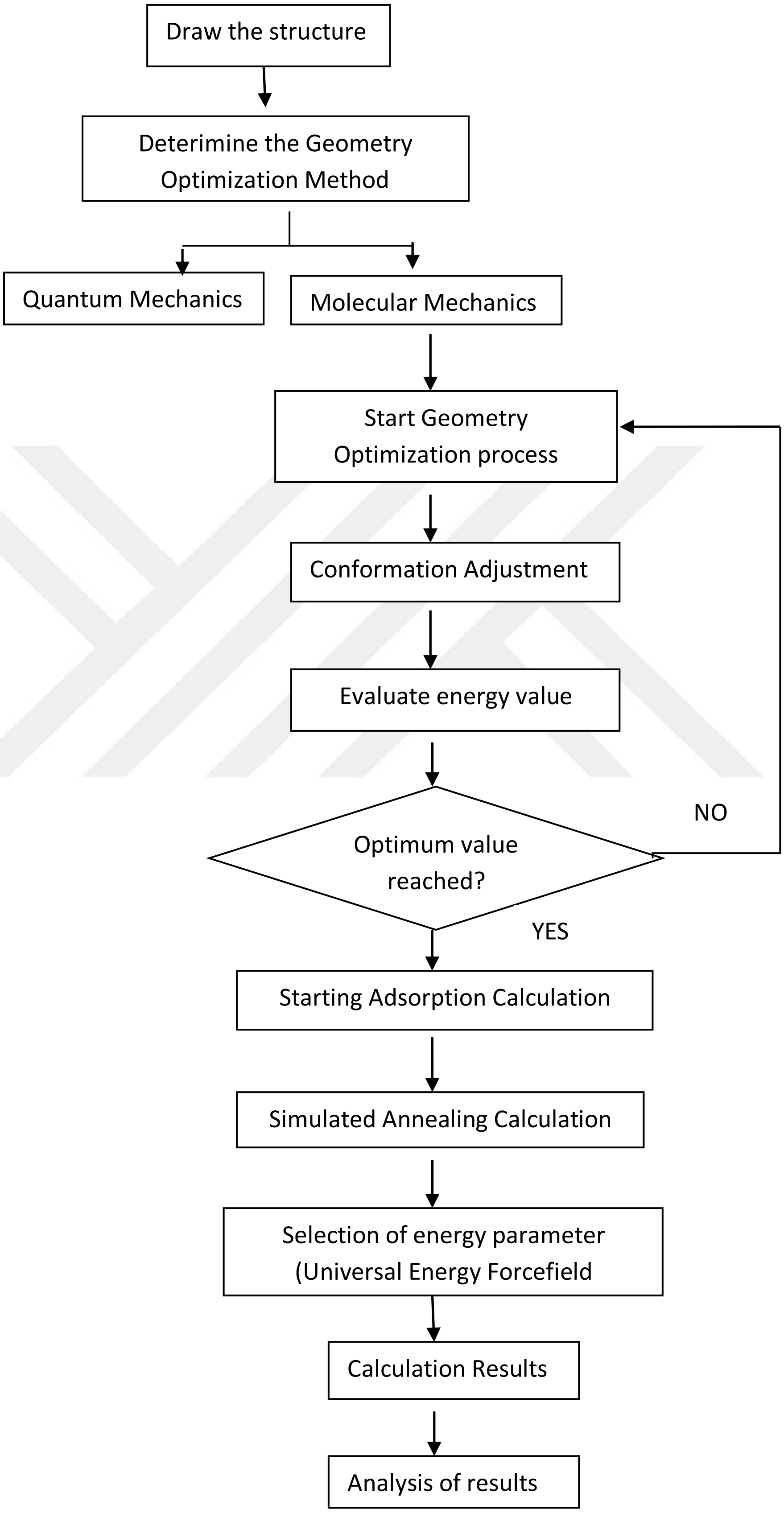

Figure 3.1 Flowchart of proposed methodology.

3.2. Chemical and Physical Properties of Rice Husk

Rice is the second most produced cereal after wheat. After rice husks are processed in plants, bran (approximately 9-10%) and husks (approximately 20%) are separated and the rice is obtained (Pourshakiba, 2012). The bran is a thin membrane that covers the rice, and as it is nutritious, it is used as animal feedstock. The husk is on the outer section, and contains silis and carbon (Pourshakiba, 2012). Figure 3.2 shows the rice paddy, and Figure 3.3 shows the process of rice husk separation.

Figure 3.2 Rice paddy

Figure.3.3. Separating the rice husk from the rice [29].

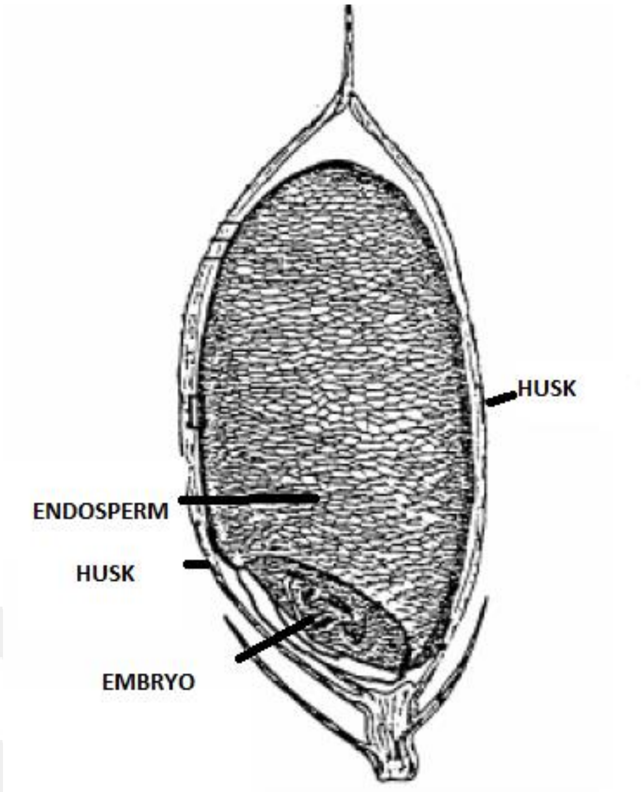

Figure 3.4 Structure of rice husk (Özgül, 1991)

The husk has four structures:

1. A rock like wavy thick layer
2. Partly lignified thick hard tissue
3. Cellular tissue which kills the fiber
4. Internal tissue, made of cells with equal dimension

While the chemical composition of the husks varies based on the geographical location, water and climate conditions, rice husks are approximately 40-45% cellulose, 25-30% lignin, 15-20% ash, 8-15% moisture (Pourshakiba, 2012). As mentioned before, 78% by weight is rice and bran, the remaining 22% is the husk and 18-22% by weight is ash.

When the worldwide rice production is taken into account, the release of the ash after the husks' incineration provides a great danger to the environment.

In the following tables typical composition and chemical composition of rice husk are given.

Table 3.1. Typical and chemical composition of the rice husk ash (Yıldız et al., 2007; Srivastava et al., 2006).

Typical composition of rice husk ash	
Cellulose	32.24%
Hemicellulose	21.34%
Lignin	21.44%
Water	8.11%
Mineral Ash	15.05%
Density (g mL−1)	0.4
Chemical composition of rice husk ash	
SiO_2	96.34%
K_2O	2.31%
MgO	0.45%
Fe_2O_3	0.20%
Al_2O_3	0.41%
CaO	0.41%

Table 3.2. Reported physicochemical characteristics of rice husk (Malik, 2003).

Bulk density (g/ml)	0.73
Solid density (g/ml)	1.5
Moisture content (%)	6.62
Ash content (%)	45.97
Particle size (mesh)	200-16
Surface area (m^2/g)	272.5
Surface acidity (meq/gm)	0.1
Surface basicity (meq/gm)	0.45

Rice husk has low bulk density and because of this large volume for storage and transport, which makes transport over long distances un-economical.

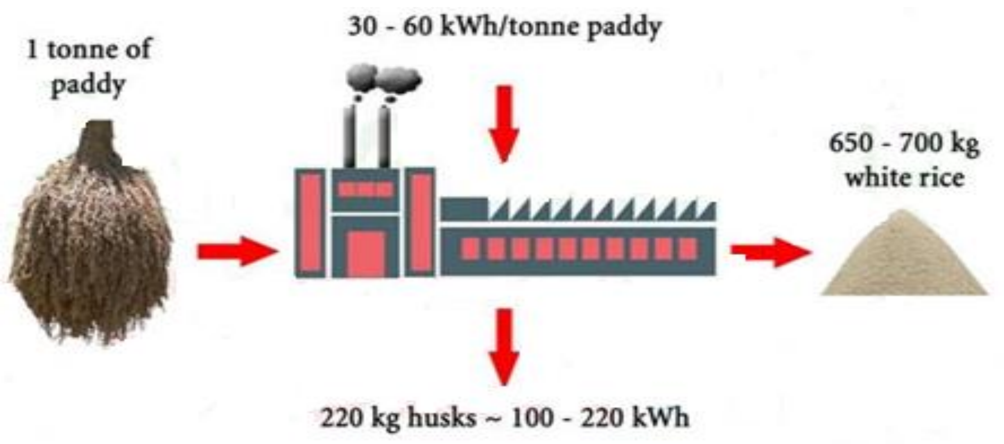

Figure 3.5 Rice husk production.

According to Figure 3.5 we obtain 650- 700 kg white rice and 220 kg husks from one ton of paddy and total 30-60 kWh energy is required per every ton of paddy.

Figure 3.6 Rice husk bulk.

3.3. Molecular Modeling

There are two basic methods in analyzing a molecule or molecular system: experimental and theoretical. Experimental procedures include NMR, X-Ray Diffraction, IR Spectroscopy, among other methods. The theoretical methods consist of analytical methods and molecular modeling (Demir, 2012). In this study, molecular modeling was used.

Molecular modeling is calculating a molecule's physical properties by means of computers (Demir, 2012). In order to calculate the physical properties, the required component is the system energy. The biggest advantage of molecular modeling when it is compared to other methods is not having to run expensive experiments, and is making a cost and time effective study (Demir, 2012). The methods to solve the problems are already coded in the system.

With molecular modeling, molecules and reactions that are difficult to observe can be assessed. Also complex structures such as, semiconductors, superconductors, plastics and ceramics have been studied by using computational chemistry (Lewars, 2003). Molecular modeling has a wide range of use in sciences and medicine industry.

In molecular modeling, there are two main methods that calculate the change in energy by different methods. They are:

-Molecular Mechanical Methods

-Quantum Mechanical Methods

  -Semi-Experimental Methods

  -Ab initio Methods,

  -Density Functional Theory

In this study, the molecular mechanical method was used. Molecular mechanics use classical physics rules and basic potential functions in order to determine the molecule structure and properties. Molecular mechanics is a quick method and can optimize large molecules like enzymes in seconds. In this method, the properties based on electronical structure are not calculated (Bulanık, 2010) Software such as AMBER; HYPERCHEM and CHARM can be used for this method.

3.4. Geometry Optimization

In scientific calculations, geometry optimization is a series of iterations performed on a molecule to obtain the minimum energy state, where the molecule is stable, or to find the intermediate products of a reaction (Eryılmaz, 2007).

The algorithm used for optimization aims to find the stationary points, where the first derivative is zero and the second derivative is negative (Yavuz, 2009). In other words, it aims to find the geometry parameters that are the regional minimum in the potential energy surface (Kolay, 2008). To carry out a geometry optimization (minimization) program starts with a set of Cartesian coordinates for a molecule and tries to find a new set of coordinates with a minimum potential energy. Because of potential energy surface is very complex, even for a molecule containing only a few dihedral angles, the molecular structure found during an optimization may be a local and not a global minimum (Fletcher, 1980). If the energy has reached a minimum or the specific structure of the structure that is being studied, the program converges and gives the calculation results. If the program does not converge, the error given is examined, the geometry data is controlled and a feasible value must be entered for the next run.

3.4.1. The optimization process

We can summarize optimization of a structure in a two step process: (Fletcher, 1980; Gill et al., 1981).

- Energy assessment

  For a given conformation energy statement must be defined and evaluated.

- Conformation adjustment

  The conformation is adjusted to find minimum energy value and it may be found after one adjustment or after thousands of iterations. The number of iteration is related to the nature of the algorithm and the size of the structure.

There are two indicators for efficiency of the optimization; first one is time needed to evaluate the energy expression and the second one is the number of iterations needed to converge to the minimum.

3.4.2. Geometry optimization algorithms

There are several standard algorithms for geometry optimization of a structure and some of these are described in this section. These algorithms are; (Fletcher, 1980).

- Steepest Descents
- Conjugate Gradient
- Newton- Raphson methods

3.4.2.1. Steepest descents

This method was founded by Magnus Hestenes and Eduard Stiefel and can be used for unconstrained optimization problems like energy optimization (Straeter, 2011).

This method is a first order minimizer and it uses the first derivative of the potential energy with respect to the Cartesian coordinates. In this method, if f function is a real function and its gradient is $\nabla f(x) = (\partial f/\partial x_1; \partial f/\partial x_2; \ldots; \partial f/x_n)$, for $x_0 \in R^n$ the line search direction can be defined along the direction of the local downhill gradient vector $v = -\nabla f(x_0)$. After this step ; this method produces a new direction that is vertical to the former gradient via the formula of $x_1 = x_0 - \alpha\nabla f(x_0)$ and this calculation continues until the program converges to the local minimum (Natali et al., 2013).

The steepest descent method is especially useful for eliminating the large nonbonded interactions often found in initial structures and required computing time for each step is minimal (Fletcher, 1980).

The steepest descents method is suitable if the configurations are not close to the minimum and the gradients are large and because of that this method can be used for the first steps of optimization. Steepest descent method has been fundamental for Newton-Raphson and other improved algorithms (Fletcher, 1980). Figure 3.7 shows the principle of steepest descent method.

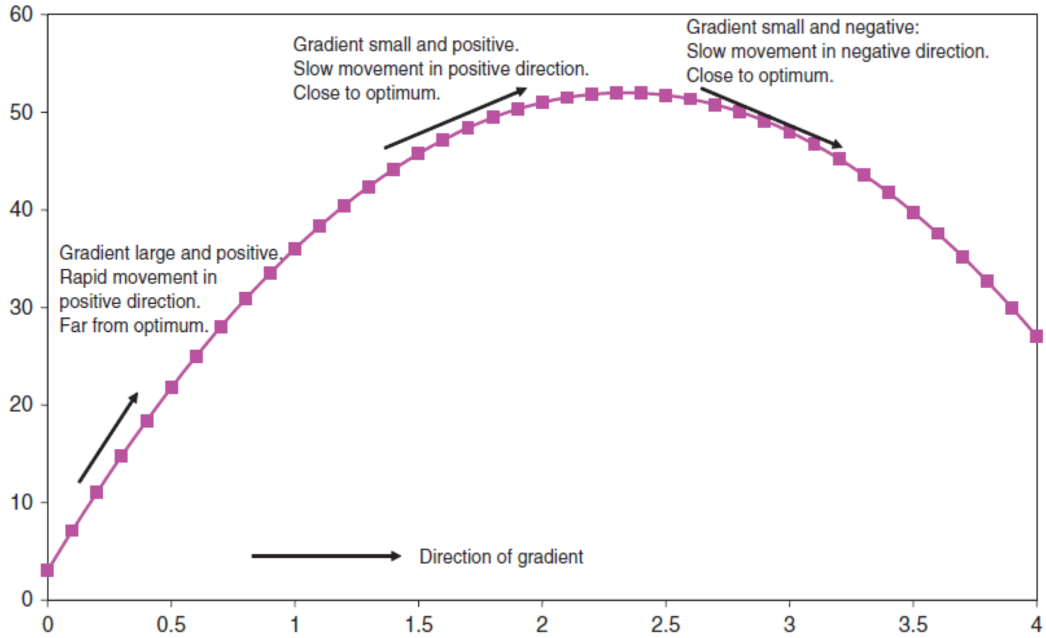

Figure 3.7 Principle of steepest descent method (Brereton, 2009).

Figure 3.7 shows basic methodology of an optimization. According to this figure we can infer that at the bottom left, because of the gradient is positive and large, optimizer will tend to positive direction. At the top of right, the gradient is small and negative, so optimizer will progress in a negative way**.** One of the disadvantages of this method is that convergence toward a minimum is very slow (Brereton, 2009).

3.4.2.2. Conjugate gradient

The conjugate gradient algorithm constructs and follows set of reciprocal conjugate directions and each successive step helps direction to achieve the minimum. This method is generally suitable for large models (Hestenes and Stiefel, 1952)

In this method, calculation formula of the new direction vector is;

$h_{i+1} = g_{i+1} + \gamma_i h_i$ Equation. 3.1.

In this formula $\mathbf{g}_{i+1}$ is a gradient at point i+1 which is orthogonal to all previous direction , and $\mathbf{h}_i$ is the preceding direction which is conjugate to all previous directions measured by a constant γ_i.

There are two methods for calculating $\gamma_{i.}$ One of them is Polak- Ribiere method and according to this method we can calculate γ_i like this;

$\gamma_i = (g_{i+1} - g_i)\, g_{i+1} / g_i^2$ Equation. 3.2.

And according to other method, Fletcher-Reeves method, γ_i can be defined like;

$\gamma_i = g_{i+1}{}^2 / g_i{}^2$ Equation. 3.3.

Differences of this method from the steepest descent are; using both the current gradient and the previous search direction to achieve to the minimum converges faster and it contains a scaling factor for determining step size near optimum.

3.4.2.3. Newton-Raphson methods

As a rule, if we have *N* variables we need N^2 independent data points to solve a harmonic function and in this condition gradient based minimizer can converge minimum in *N* steps. But if second-derivative information could be determined, the optimization process can finish in one step, because each second derivative is an $N \times N$ matrix. This is the algorithm behind the Newton-Raphson method. The mathematically expression of how this method finds the nearest minimum is; (Peng and Schlegel, 1993).

$\mathbf{r}_{min=}\ \mathbf{r}_0 - A^{-1}(\mathbf{r}_0) . \nabla E(\mathbf{r}_0)$ Eq. 3.4.

In this equation;

$\mathbf{r}_{min}$ is the predicted minimum, t

$\mathbf{r}_0$ is an arbitrary starting point,

$\mathbf{A}(\mathbf{r}_0)$ is the matrix of second derivatives of the energy with respect to the coordinates at $\mathbf{r}_0$ which also known as the Hessian matrix

$\nabla E(\mathbf{r}_0)$ is the gradient of the potential energy at $\mathbf{r}_0$.

There are some drawbacks of this method such as; (Straeter, 2011).

- Determining the terms in the Hessian matrix is a difficult and costly process.

- The optimization of a system may be very difficult if the structure is far from the minimum.

-For complicated and large systems calculating and inverting a $N \times N$ matrix can become impractical.

There is two different type of Newton - Raphson method such as quasi-Newton and truncated Newton methods. The general algorithm for this method is described in seven steps like as: (Peng and Schlegel, 1993; Eade and Robb, 1981).

Step 1. Offer an initial predicted r_0.

Step 2. Start converging process.

Step 3. Determine Hessian **A** matrix which is defined in positive value.

Step 4. Calculate search direction.

Step 5. For decreasing energy to a sufficient value evaluate an appropriate step length, λ_k,

Step 6. Increase the coordinates: $x_{k+1} = x_k + \lambda_k p_k$

Step.7 Go to step 2

We can differentiate two Newton methods depends on the calculation method of A, determining technique and accuracy value of search direction and how carry out the line search.

Important issues for optimization calculations

- First of all, accuracy of structure which wanted to be simulated is very important.

- Using a faster computer and effective optimization algorithm is also very important.

We must consider some issues like, when we should use alternative algorithm, importance of minimum energy form of structure, used gauge for testing stability of the optimization algorithm (Eade and Robb, 1981).

Two convergence criteria can be used for optimization calculation: the root-mean-square gradient and the number of optimization cycles. Root-mean-square gradient can be used for terminating optimization process, because it is difficult to predict how many cycles are needed for an adequate geometry optimization. Cycle number can be used as a termination when mixing optimization algorithms used. Gaussian software automatically calculates a default number of cycles as 15 times the number of atoms.

3.4.3. The Modeling Tool for Geometry Optimization

In this section, the molecular structures of the rice husk and polyacrylamide were modeled. Afterwards, the adsorbent was prepared from rice husks and polyacrylamide, and the probable structures that would occur when Cd^{2+} was adsorbed was determined and the start-up geometries were made in the Gaussian 09 software. The menus seen in the figures (Figure 3.7-3.10) were chosen and the necessary calculations took place. The required .gif files were prepared with the Gaussian 09 software.

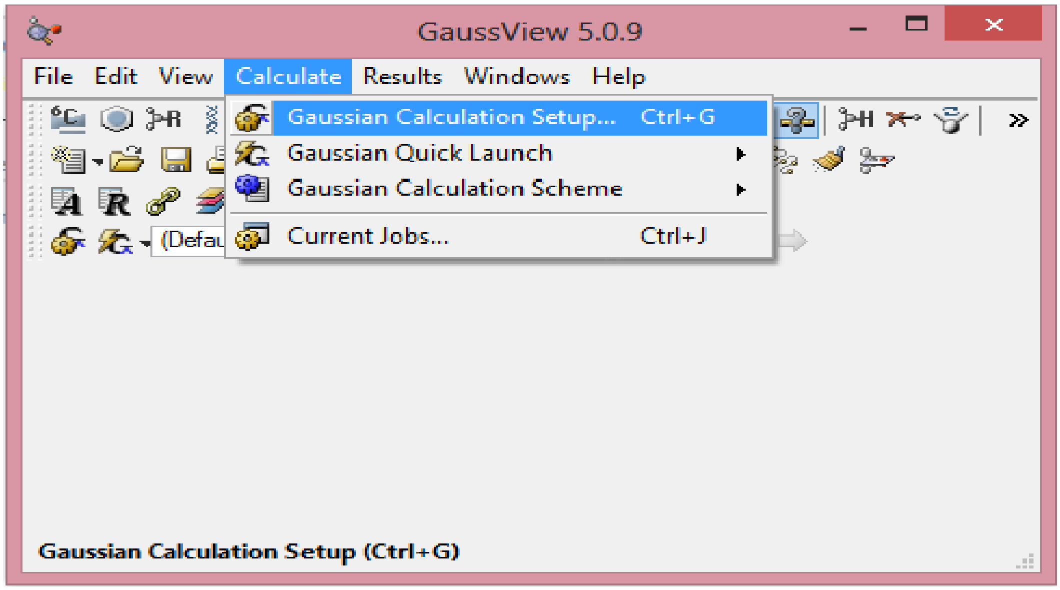

Figure 3.8 Starting calculations on Gaussian 09.

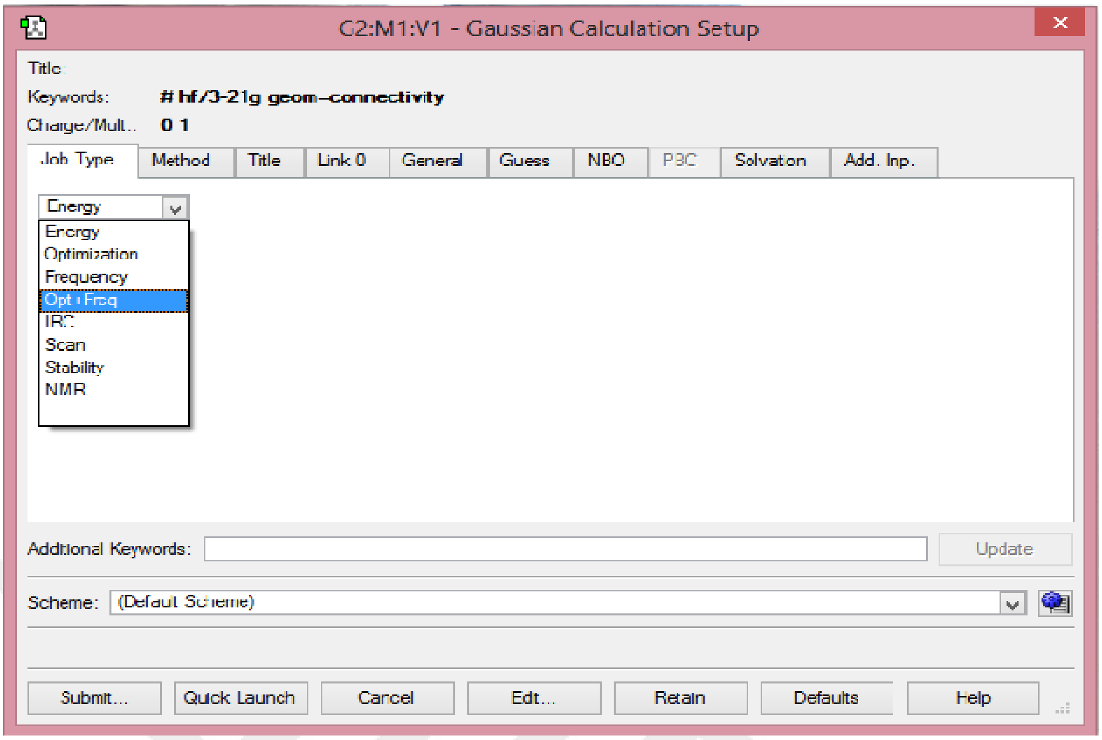

Figure. 3.9 Making required choices for optimization and frequency calculations with Gaussian 09.

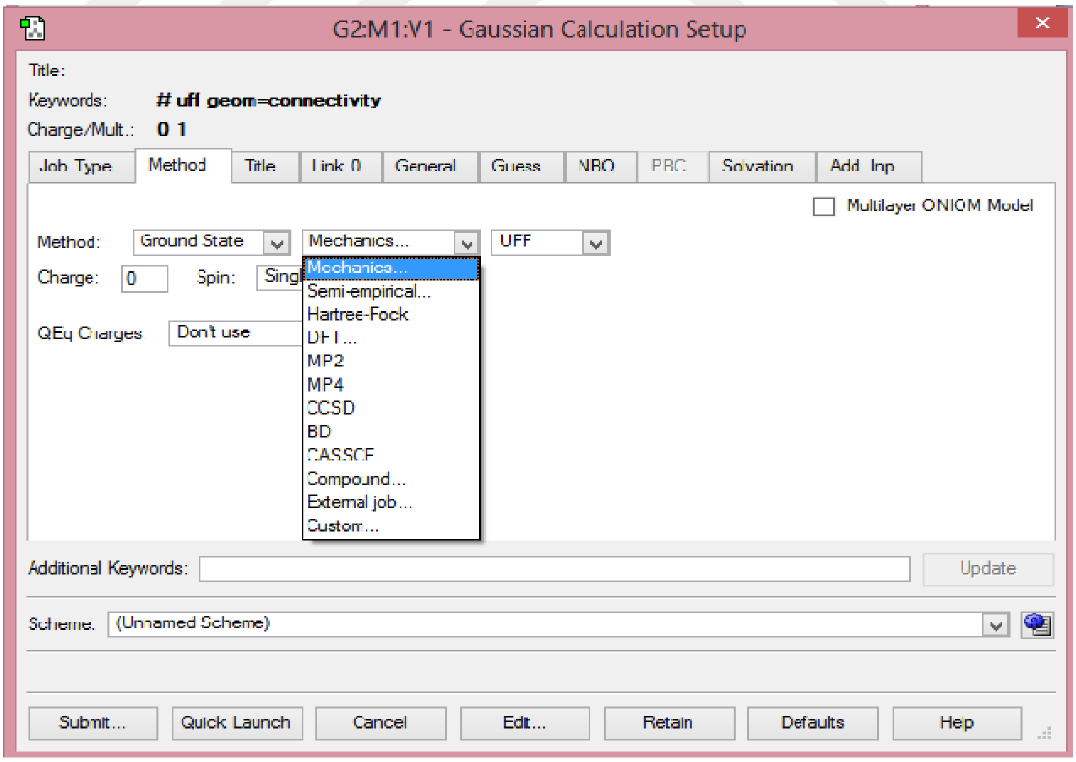

Figure 3.10 Selection of methods and basis sets for optimization and frequency calculations on Gaussian 09.

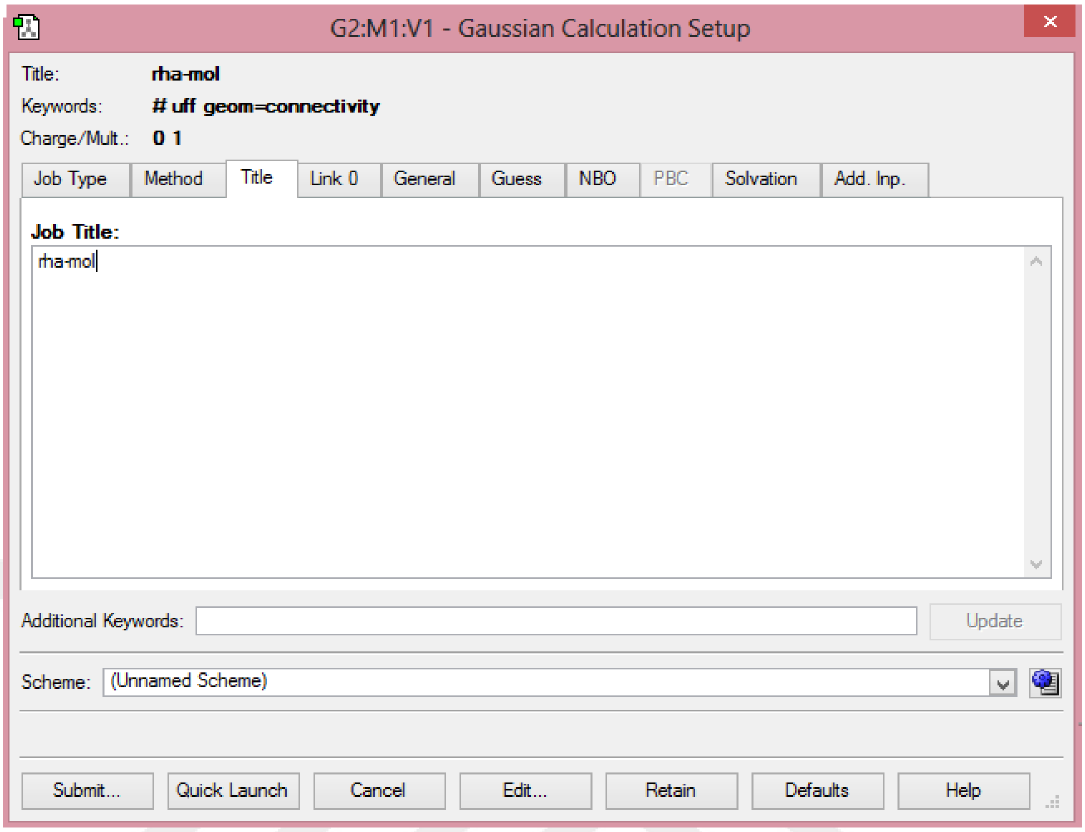

Figure 3.11 Title name selection before submitting the process

3.5. Adsorption Simulation

In this section we used a computer program, Material Studio 6.1, for examining adsorption property of polymer coated rice husk. We calculated adsorption energies of our possible 36 structure an unmodified rice husk with aid of Adsorption Locater tool of this program. Afterwards, the adsorption energies in which the Cd^{2+} ion binds in single, double, quadruple and sextant bonds and finally the structure with the highest adsorption energy was determined.

3.5.1. Adsorption Locator

Adsorption Locator is used to simulate adsorption of pure adsorbate or adsorbate mixtures and to find low energy adsorption regions on adsorbent.

We can summarize the steps for setting up and running an Adsorption Locator calculation such as; (Cerný, 1985; Frenkel and Smit, 2002).

Step 1. Ready the structure which will be simulated

Step 2. Identify the adsorption area

Step 3. Finding possible adsorption areas

Step 4. Start the adsorption modules on the program used

3.5.2. Theories used for Adsorption Simulation

There are three theories behind the adsorption locater modules of the program which we used to simulate the adsorption of Cd^{2+} ions to rice husk adsorbent. These theories are: generation of substrate-adsorbate configurations, Metropolis Monte Carlo method and simulated annealing. We will give brief information about these methods in this section.

3.5.2.1. Generation of substrate-adsorbate configurations

In Adsorption Locator simulation, the nominee substrate-adsorbate configurations are sampled from a population and the probability of a configuration, *m*, in the population is calculated by the equation 3.5. : (Frenkel and Smit, 2002).

$P_m = C\, e^{-\beta E_m}$ Equation. 3.5

In this equation; C is an optional normalization constant, β is the mutual temperature, and E_m is the total energy of configuration m.

The β can be determined with the aid of the equation below:

$\beta = 1/\, k_B T$ Equation. 3.6.

In this equation, k_B is the Boltzmann constant and T is the absolute temperature.

E_m, total energy of configuration m, can be determined according to equation 3.7.:

$E_m = E_m^{AA} + E_m^{AS} + U_m^{A}$ Equation. 3.7.

In this equation:

E_m^{AA} is the intermolecular energy between the adsorbate molecules, E_m^{AS} is the interaction energy between the adsorbate molecules and the substrate, and U_m^{A} is the total intermolecular energy of the sorbate molecules.

In an Adsorption Locator simulation, first phase is to adsorb the determined number of adsorbate molecules of each constituent. This step continues by a series of insertion steps and equilibration runs until the defined loading has been achieved. We can seperate the simulation process into an equilibration and a production step (Frenkel and Smit, 2002).

3.5.2.2. Metropolis Monte Carlo method

The basic algorithm of Metropolis Monte Carlo method, which is the most widely used Monte Carlo method, was developed in 1953 by N. Metropolis and advanced in 1970 by W. K. Hastings (Metropolis et al., 1953).

Monte Carlo simulations are widely used to compute the thermodynamic properties of a molecule or a system of molecules, and have been employed generally in the study of the structure of liquids and solutions. It is repeated application of a computational algorithm that generates a new configuration from the current configuration. This simulation method uses a statistical sampling technique to generate configurations (Allen and Tildesley, 1987).

The method used in Adsorption Locator generates a set of configurations, m, n, ..., from a population and the probability of transition from m to n is π_{mn}. It means that if configuration n is sampled with a probability ρ_n, then $\rho_m\pi_{mn}$ of them are transformed to m and vice versa. There must be a net flow through each configuration and with consideration of this information equilibrium state can be determined with equations below: (Metropolis et al., 1953).

$$p_n\, \pi_{mn} = p_n\, \pi_{nm} \qquad \text{Equation 3.8.}$$

In the Metropolis Monte Carlo method, the acceptance probability, P_{mn}, can be calculated with aid of formula in Equation 3.9,

P_{mn} = min [1, $\alpha_{nm}\ \rho_n / \alpha_{mn}\ \rho_m$]   Equation 3.9.

In this formula, α_{mn} *is* trial configurations probability, P_{mn} is proposed configurations (n) probability and the original configurations (m) probability is 1-P_{mn}. We can simplify this equation with the consideration $\alpha_{mn}= \alpha_{nm}$, because in the Metropolis Monte Carlo method, trial configurations are created without bias and the formula for acceptance probability changes to:

P_{mn} = min [1, ρ_n / ρ_m]   Equation 3.10.

With integrating the Equation. 3.8 and Equation. 3.10 we obtain Equation. 3.11:

P_{mn} = min $\{1 , -\beta(E_n - E_m)\}$ Equation 3.11.

In this equation β is the mutual temperature, E_n is the total energy of configuration n and, E_m is the total energy of configuration m. According to this equation, transitions to a low-energy configuration ($E_n < E_m$) are desired.

If we summarize the procedures of Metropolis method, a randomly selected atom attempts to move by a random distance in a random direction and the energy change depend on this move is calculated. If the energy change is negative, the move is accepted, and the energy of the system is added to the currently running average. If the energy change is positive, then the move is accepted with probability of calculated P_{mn} value. A big positive change in energy means that the move will less likely be accepted. If a move is rejected, then the energy of the old configuration is again added to the average. In our package program, the atoms are not chosen randomly, but instead, each atom is moved once per Monte Carlo step.

There are four stages in Metropolis Monte Carlo method for a standard ensemble: conformer, rotation, translation, and regrowth. In conformer step; a randomly selected conformation is altered for confirmation of specific adsorbate. In rotation step; this adsorbate is rotated around its center of geometry. In translation step; this adsorbate is translated by a determined distance and in regrowth step this specified adsorbate is removed and a new adsorbate is replaced with a random orientation and random conformation (Metropolis et al., 1953).

We can summarize the Metropolis algorithm in Monte Carlo simulations with this steps : (Newman and Barkema, 1999).

Step 1. Start with configuration which has an energy value of E_i.

Step 2. Asses a trial state with changing one spin of the initial configuration.

Step 3. Calculate the energy of the trial state, E_f.

Step 4. Determine $\Delta E = E_f - E_i$.

Step 5. If $\Delta E \leq 0$, accept the trial configuration, and go to Step 7.

Step 6. If $\Delta E > 0$, calculate the acceptance ratio of new configuration ($\omega = e^{-\beta \Delta E}$)

Step 7. Compare acceptance ratio with a random number r.

If $r \leq \omega$ accept the new configuration,

If $r \geq \omega$ reject the new configuration.

Step 8. Try different values.

Step 9. Repeat the steps between step 2 and step 7 for obtaining a sufficient representation of configurations.

Step 10. Complete Monte Carlo cycle with summing all spins.

Step 11. Divide the different prospected values with the total number of cycles.

We can summarize the parameters of Monte Carlo Simulation such as;

1- Initial Configurations;

It is not required to begin with an energy minimized structure; a random configuration could be used, but, in order to minimize processing time it will be preferable to begin with a physically reasonable choice.

2- Temperature;

The role of simulation temperature in Monte Carlo simulations is firstly to modulate the strength of intermolecular interactions, and also determines the average kinetic energy. Kinetic energy contributes a fixed amount to averaged potential energy to give the average total energy.

3- Step Size and Acceptance Ratio

The step size is the maximum allowed atomic displacement used in the generation of trial configurations. According to the researches about the optimum value of the acceptance ratio is a value around 0.5. When the value of the step size determined as 0.05 Angstroms, acceptance ratio about 0.5 will be obtained, which means that about 50% of all moves are accepted. Increasing the size of step may lead to the acceptance ratio will, in general, decrease and in the other smaller displacements generally lead to higher acceptance ratios.

4- Initial Phase and Equilibration

The first phase of optimization process in general statistically insignificant configurations. During optimization period, the potential energy may either increase or decrease, depending on the starting point. The number of steps required before equilibration point and equilibrium averages can be accumulated is strongly dependent on the system, the step size, the starting point, and the temperature of the simulation.

5- Heating and Cooling

In Monte Carlo simulations heating and cooling phases are optional and not often used.

3.5.2.3. Simulated annealing

Simulated annealing, a metaheuristic algorithm for approximation to the global minimum, name of it is referring the annealing operation in metallurgy. In this process microcrystalline structures are heated and then slowly cooled. Heating temperature and cooling rate is very important in this process to obtain big sized crystallite. For any function, the object function can be accommodate to the energy of the crystal, function variables correlated with the atom configuration, and the minimum energy of the configuration can be related with the steady state mode of crystal molecules (Kirkpatrick et al., 1983)

In minimizing process of the objective function, a set of possible states are evaluated. And this optimization process consists of repeatedly perturbing singular values of this possible states in order to achieve to a global objective function, Q. At each step, evaluated new value of the function is compared with the current value. Acceptance of this new values is depends on Boltzmann-type exponential probability distribution controlled by a temperature parameter T. The acceptance probability p of a specified configuration is: (Dafflon et al., 2009)

$p = 1$, if $Q_{new} < Q_{current\ or}$

$p = e^{(Qnew - Qcurrent) / T}$, in other case

If we increase the value of control parameter, T, it leads to accept to the unfavorable perturbations or in other words it causes to accept the steps in wrong way. To find a global minimum, this sampling method must be combined with a gradually decreasing control parameter.

A flowchart of the general methodology of simulated annealing simulation process is shown in Figure 3.12 (Deutsch, 2002; Kelkar and Perez, 2002; Tronicke and Holliger, 2005).

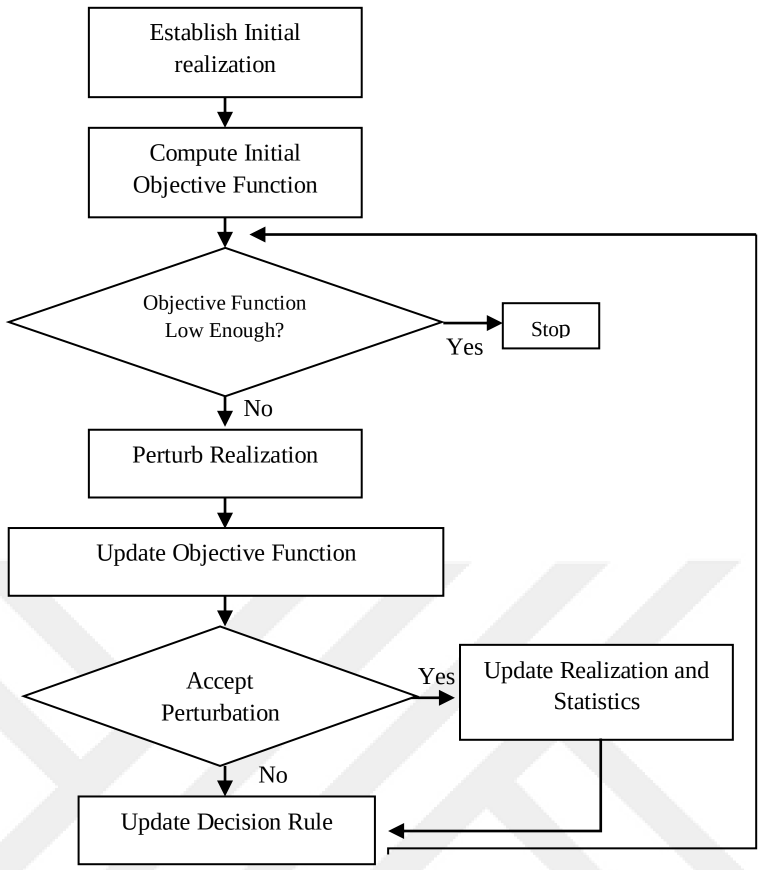

Figure 3.12. Flowchart of the general methodology of simulated annealing simulation process.

The simulated annealing method uses a Monte Carlo sampling for searching global minimum. At the end of the first cycles of the process, the system will have achieved to a local minimum and with repeating temperature cycles this can converges solutions which are closer to global minimum (Kirkpatrick et al., 1983)

3.5.3. The Modeling Tool for Adsorption Simulation

In this section we used a package program called Material Studio 6.1 which is a simulation program that enables the engineer to develop new materials in various industries. Adsorption Locater tool was used for calculations in our study. There are some benefits using a computer program instead of experimental study in adsorption calculation studies such as; reducing the cost and time , developing a new, preferable performing and cost effective materials can be done more quick then experimentation, reduce workload of researcher and rising up productivity.

The formula for calculation to adsorption energy is shown below (Acemioğlu, 2004).

$\Delta G^o = -RT \ln K_c$ Eq. 3.12.

$\ln K_c = - \Delta H^o /RT + \Delta S^o /R$ Eq. 3.13.

In this formula,

ΔG^o ; is standard Gibbs free energy,

ΔH^o ; standard enthalpy

ΔS^o ; standard entropy.

ΔH^o and ΔS^o can be determined respectively, with the slope and the intercept point of the graph of ln K versus 1/T and K_c is adsorption equilibrium constant.

Adsorption equilibrium constant can be calculated with the formula below; (Acemioğlu and Alma, 2001).

$K_c = C_{ads} / C_e$ Eq. 3.14.

In there, C_{ads} is the concentration of adsorbed substance at the equilibrium point (mg/L), C_e is the concentration of the substance remaining at the equilibrium point (mg/L).

In figures below we showed that which tools we selected for adsorption calculations.

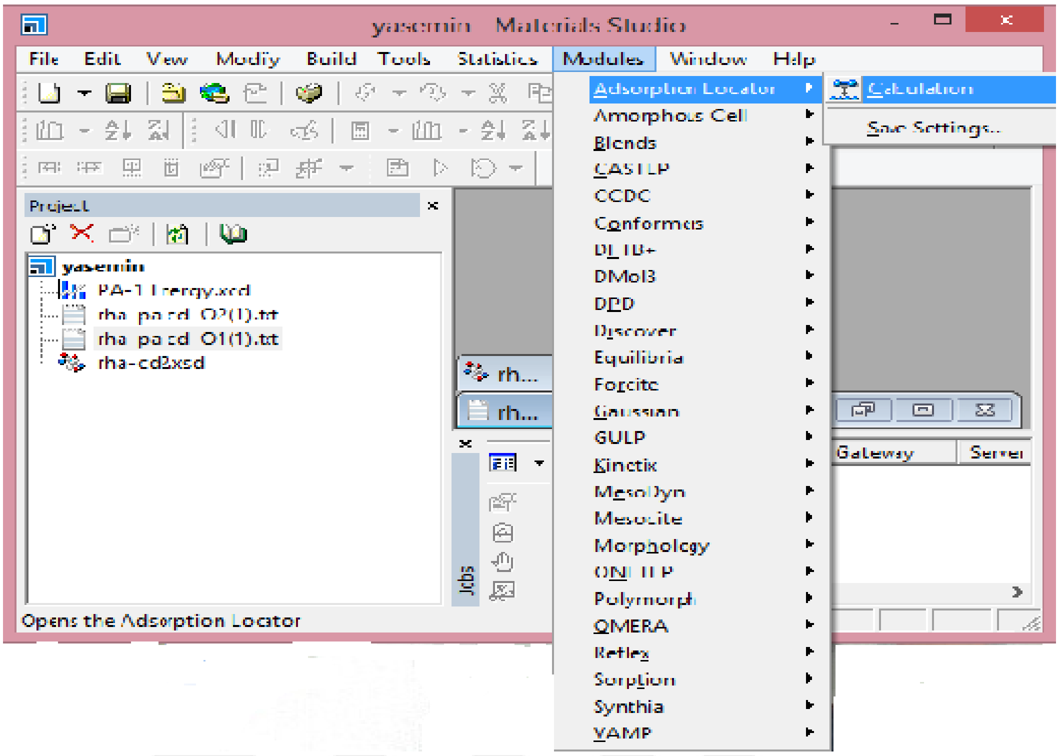

Figure 3.13 Starting calculations on Adsorption Locator at Material Studio 6.1

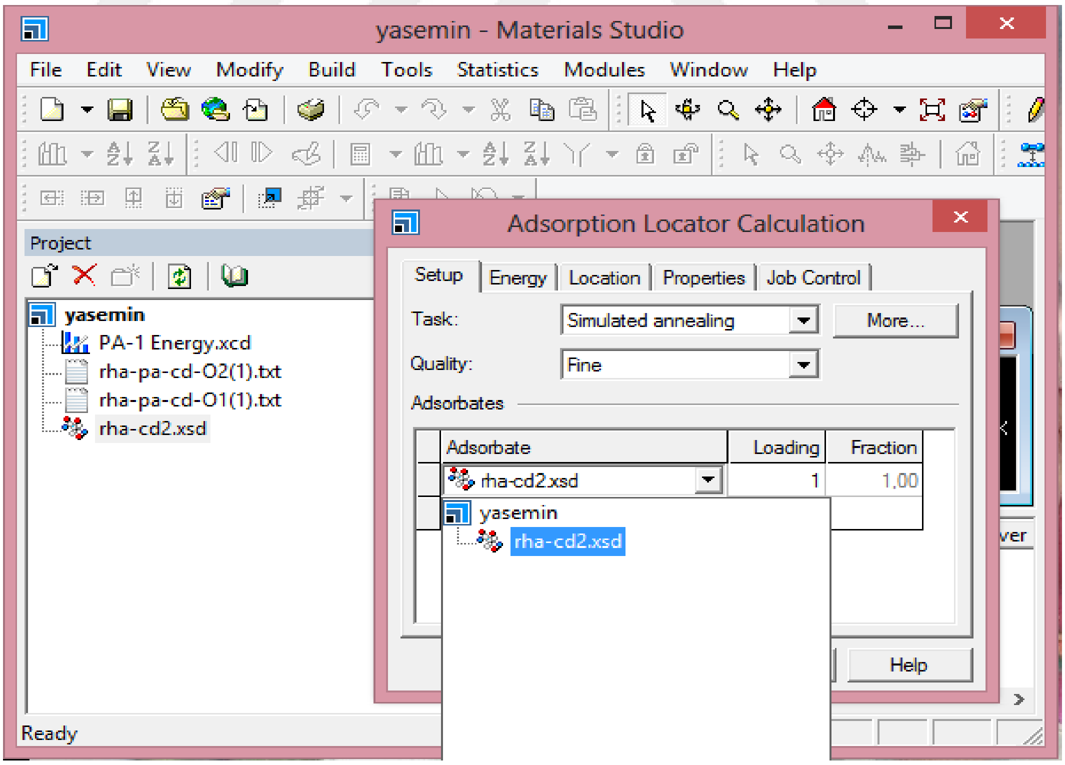

Figure 3.14 Making required choices for adsorption calculations with Material Studio 6.1

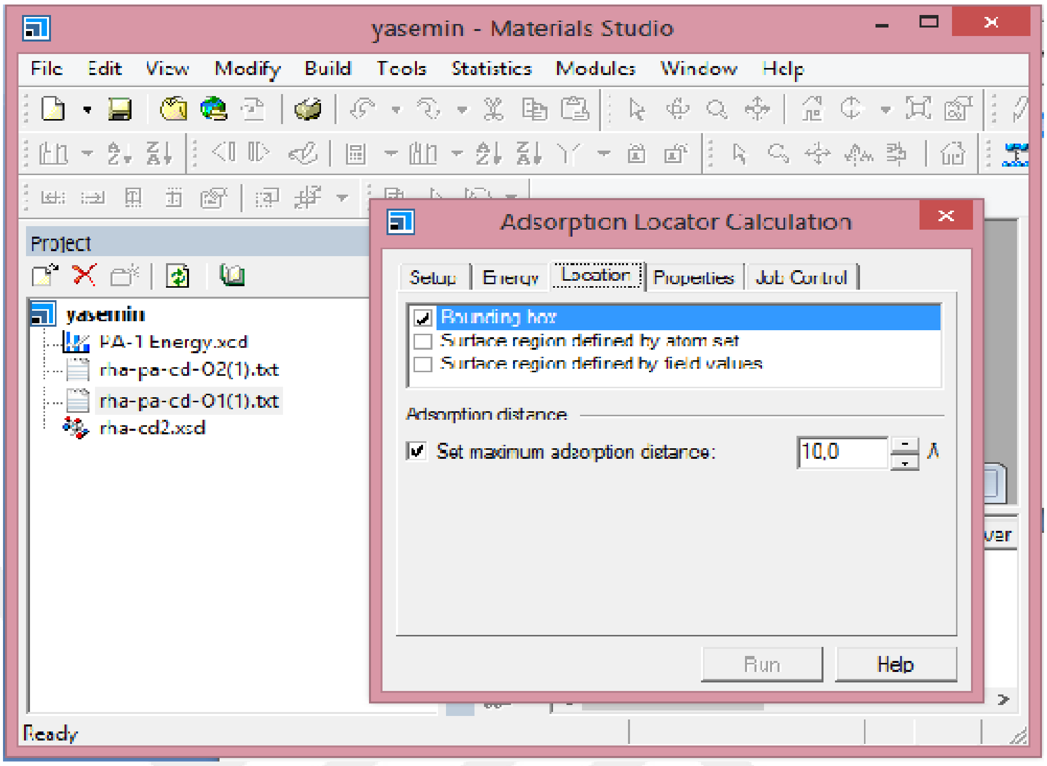

Figure 3.15 Selection of adsorption location

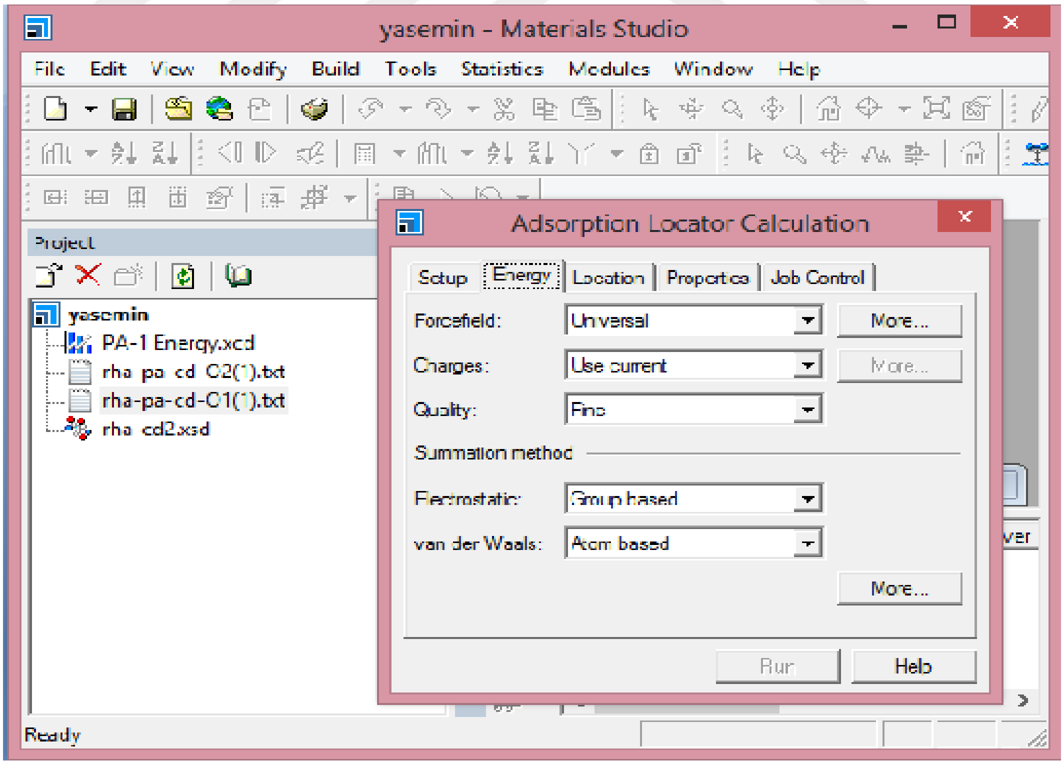

Figure 3.16 Selection of energy forcefield type

CHAPTER 4

4. RESULTS and DISCUSSION

4.1. Results of Geometry Optimization

In this section, the binding mechanism of Cd^{2+} to the adsorbent, made from rice husks and polyacrylamide (which has a wide range of use) was attempted to be explained. The following figure shows the reaction mechanism of prepared adsorbent.

$$\underbrace{\mathbf{R} + \mathbf{CH_2{=}CONH_2} + \mathbf{CH_2(NHCOCH{=}CH_2)_2}}$$

$$\xrightarrow{\mathbf{70°C,\ K_2S_2O_8}}$$

$$\mathbf{RP\text{-}CONH_2}$$

$$\xrightarrow{\mathbf{100°C,\ Toluene}}$$

$$\mathbf{RP\text{-}CONHCH_2CH_2NH_2} + \mathbf{(CH_2CO)_2O}$$

$$\xrightarrow{\mathbf{pH{:}4.0}}$$

$$\mathbf{RP\text{-}CONH(CH_2)_2NHCO(CH_2)_2COOH}$$

RP: polymer coated absorbent (rice husk)

Figure 4.1 Reaction mechanism of prepared adsorbent (Sharma et al., 2007).

This mechanism shows the structure of the adsorbent that is to be used in Cd^{2+} adsorption. The R in the adsorbent denotes the rice husk. Both cis and trans variations of polyacrylamide have been considered. The difference between the structures is: if the similar groups next to the double bond are in the same direction, it is cis isomer; if they are in opposite directions then it is called trans isomer.

After the structure of the rice husk and the prepared adsorbent was determined, the next step was finding the probable parts the Cd^{2+} would bind to the adsorbent, show the possible molecular structures and then to perform the geometry optimizations to find the most stable structure by the aid of package program that we used. The most stable structure would be the structure with the lowest optimization energy. After these procedures, the part that Cd^{2+} binds to the structure can be determined. While these probable structures were being determined, the functional groups that connect the metal ion to the biomaterial surface, which generally are amine ($—NH_2$), carboxylate (—COO), thiols (—SH), phosphate (PO_4^{3-}), and hydroxyl (—OH) were considered, and the single, double, quadruple and sextet bonds were studied (Çelekli and Bozkurt, 2011).

Energy expression or target function is the equation that describes the potential energy surface of a particular structure as a function of its atomic coordinates. The potential energy of a geometry for a molecule is described as a sum of bonded (E_R, E_θ , E_Φ , E_w) interactions and nonbonded (E_{vdw} + E_e) interactions: (Rappié et al., 1992).

$$E = E_R + E_\theta + E_\Phi + E_w + E_{vdw} + E_e \qquad \text{Eq. 4.1.}$$

E_R = the valence interactions consist of bond stretching

E_θ = Angle bend term

E_Φ= Torsional term

E_w= Inversion parameter

E_{vdw} = Van der waals energy

E_e = Electrostatic energy

As this energy value is not possible to calculate by hand, the software was used for the calculation.

The table below shows the calculated optimization energies that are a resulted from geometry optimization. The figures below show the optimized figures of rice husk, the adsorbent made with polyacrylamide, and the most stable Cd^{2+} bound molecule.

If we want to explain the depictions in the table; rha-pa-cd-O1(1) is the primary situation where the Cd^{2+} ion has a single bond with an O atom, rha-pa-cd-O1(2) , rha-pa-cd-O1(3), rha-pa-cd-O1(4) depicts that the Cd^{2+} ion has 4 single bonds with different O atoms, rha-pa-cd- O2 (3) shows one of the four situations where the Cd^{2+} ion has a double bond with O atom. Numbers next to the atom shows if the bonding is single, double, quadruple or sextet, while the numbers in parenthesis indicate how many different ways of bonding in these numbers. All of the possible structures' geometries are given in Appendix 1.

Table 4.1. Optimization energies of rice husk, adsorbent, polymer and all possible Cd^{2+} bound molecules.

Sructures	Optimization Energies(kcal/mol)	Structures	Optimization Energies (kcal/mol)
rha-pa	67.5779	rha-pa-cd-N2(6)	77.1563
rha-pa-cd-O1(1)	65.2931	rha-pa-cd-N2(7)	80.2859
rha-pa-cd-O1(2)	65.3515	rha-pa-cd-N2(8)	97.8916
rha-pa-cd-O1(3)	65.6729	rha-pa-cd-N2(9)	95.4197
rha-pa-cd-O1(4)	65.7682	rha-pa-cd-N2(10)	74.6598
rha-pa-cd-N1(1)	64.3919	rha-pa-cd-N2(11)	69.8365
rha-pa-cd-N1(2)	64.3602	rha-pa-cd-N2(12)	64.2507
rha-pa-cd-N1(3)	63.3987	rha-pa-cd-N4(1)	155.2172
rha-pa-cd-N1(4)	65.8272	rha-pa-cd-N4(2)	127.9537
rha-pa-cd-N1(5)	63.7483	rha-pa-cd-N4(3)	128.1762
rha-pa-cd-N1(6)	65.3886	rha-pa-cd-N4(4)	139.7167
rha-pa-cd-N1(7)	65.2708	rha-pa-cd-N4-O2(1)	351.9492
rha-pa-cd-N1(8)	65.3106	rha-pa-cd-N4-O2(2)	329.12
rha-pa-cd-O2(1)	67.4614	rha-pa-cd-N4-O2(3)	354.1034
rha-pa-cd-O2(2)	69.7635	rha-pa-cd-N4-O2(4)	324.722
rha-pa-cd-N2(1)	82.9876	rha-pa-cd-O2(3)	69.5696
rha-pa-cd-N2(2)	82.2313	rha-pa-cd-O2(4)	74.3879
rha-pa-cd-N2(3)	88.1641	pa-cis	10.7919
rha-pa-cd-N2(4)	81.5027	pa-trans	10.4175
rha-pa-cd-N2(5)	72.5546	Rha	23.0167

Based on the graph drawn from this table it can be realized that the structures in which the Cd^{2+} ion makes single bonds has lower optimization energies. In this case, it can be said that structures in which Cd^{2+} ion bonds with the H ions from the O and N atoms are more stable.

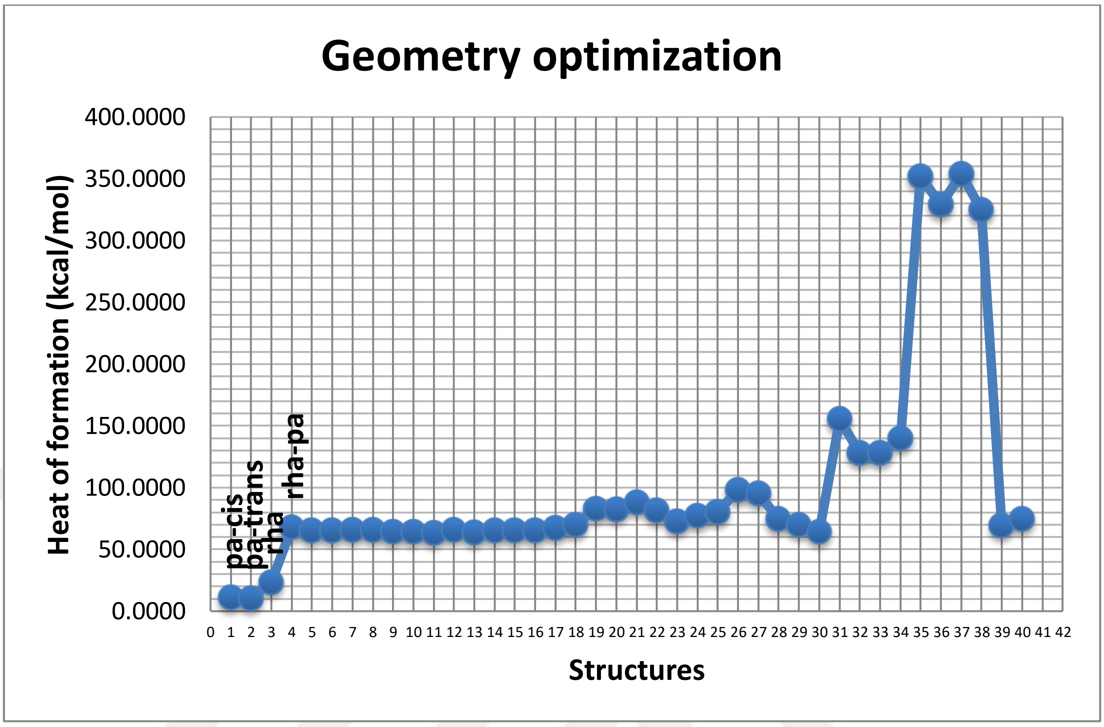

Figure 4.2 Optimization energies of rice husk, adsorbent, polymer and all possible Cd^{2+} bound molecules.

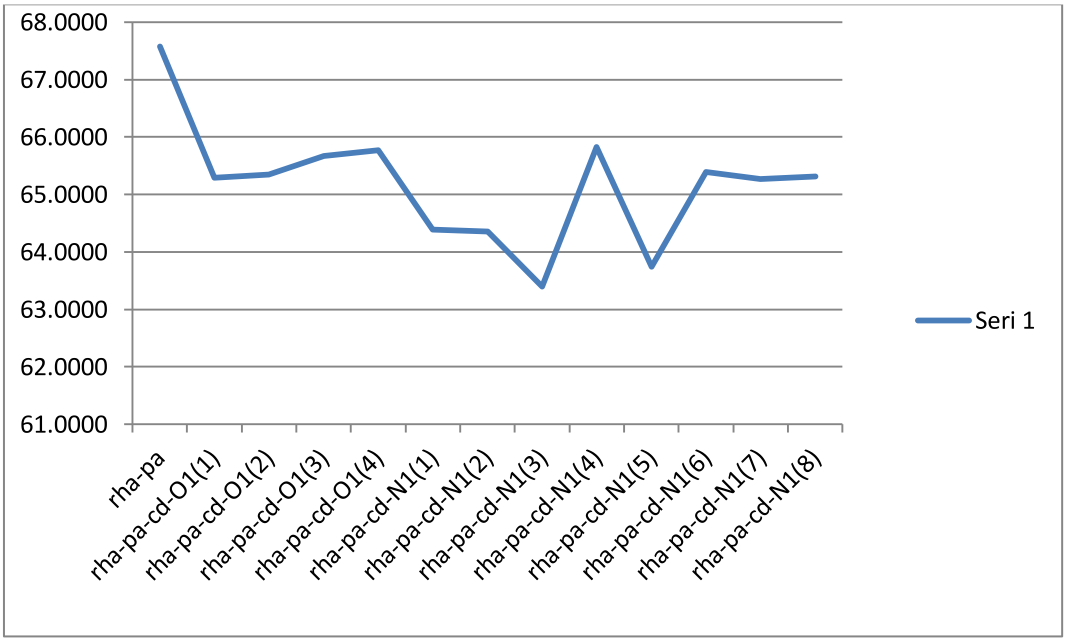

Figure 4.3 Optimization energies of the structures in which the Cd^{2+} ion makes single bonds.

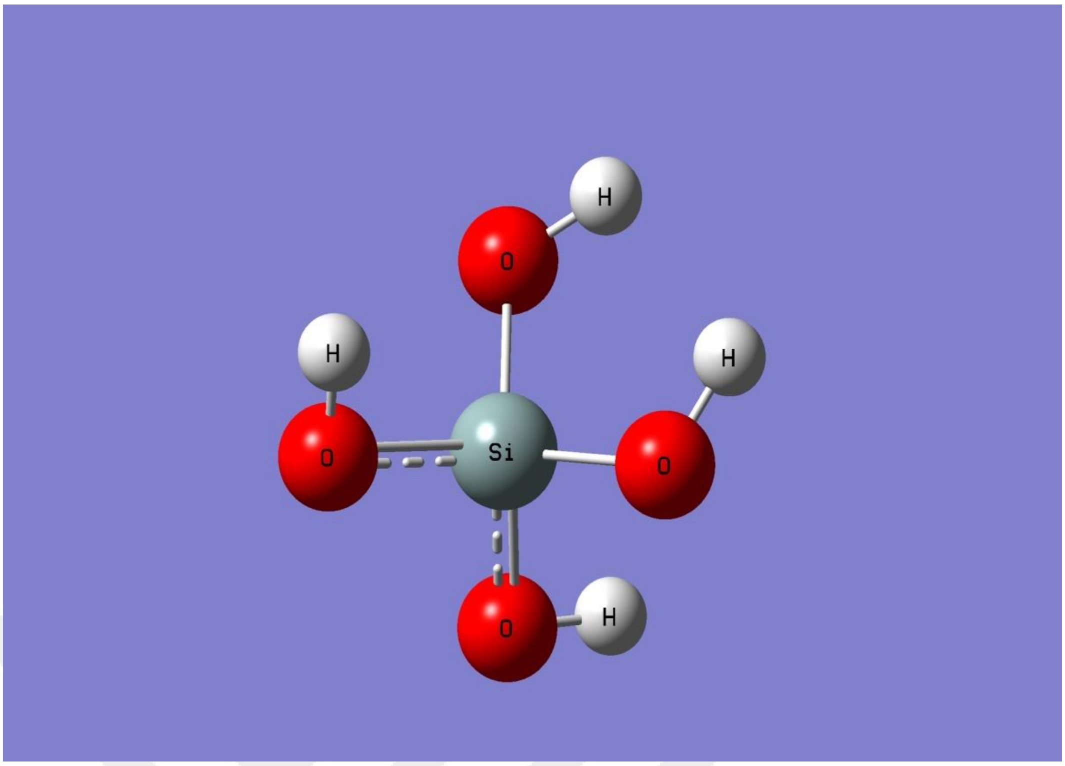

Figure 4.4 Molecular projection of the optimized rice husk molecule.

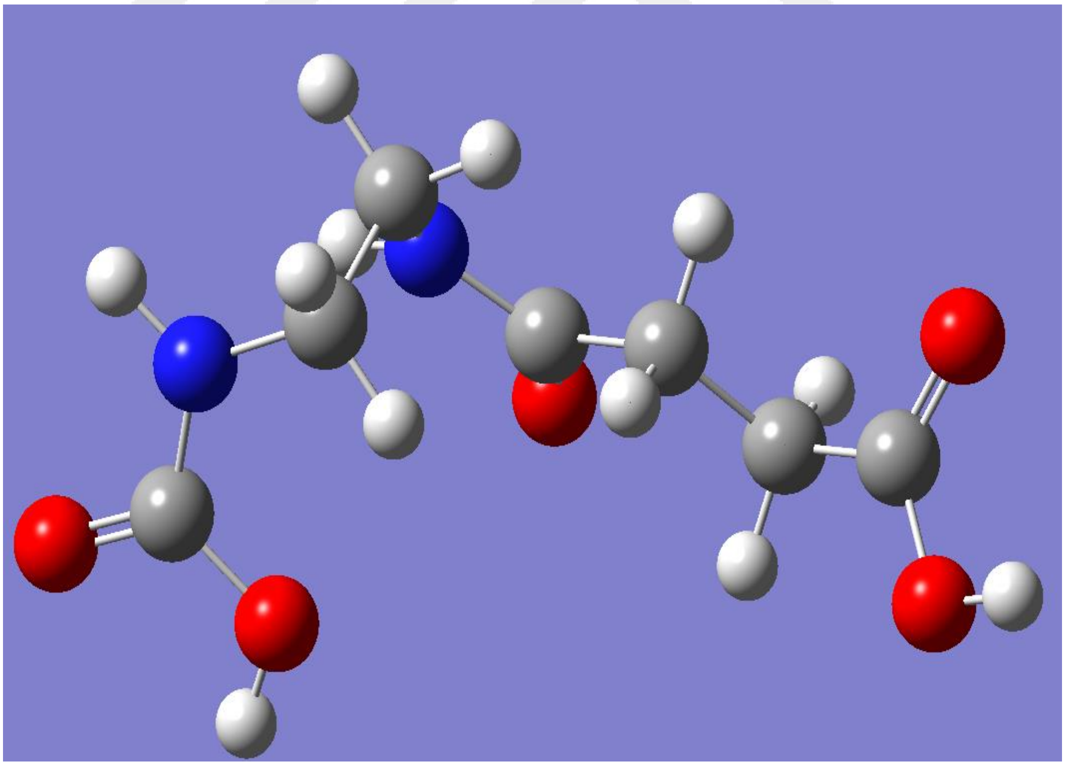

Figure 4.5 Molecular projection of the optimized cis form of polyacrylamide molecule.

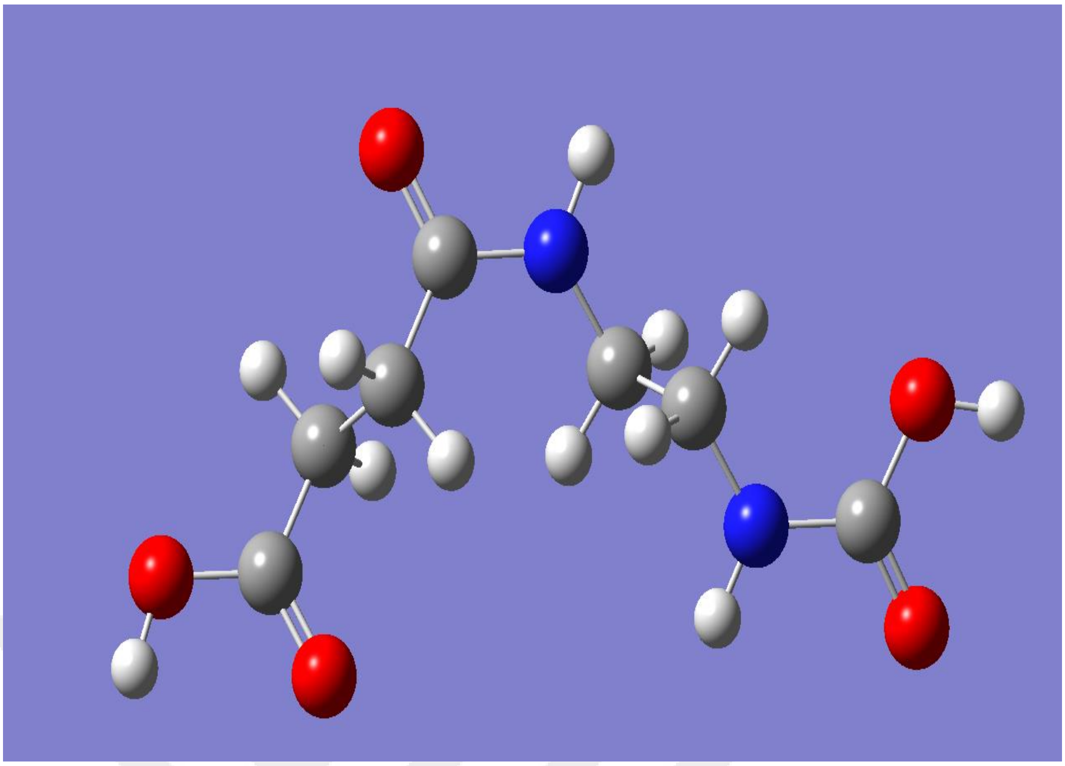

Figure 4.6 Molecular projection of the optimized trans form of polyacrylamide.

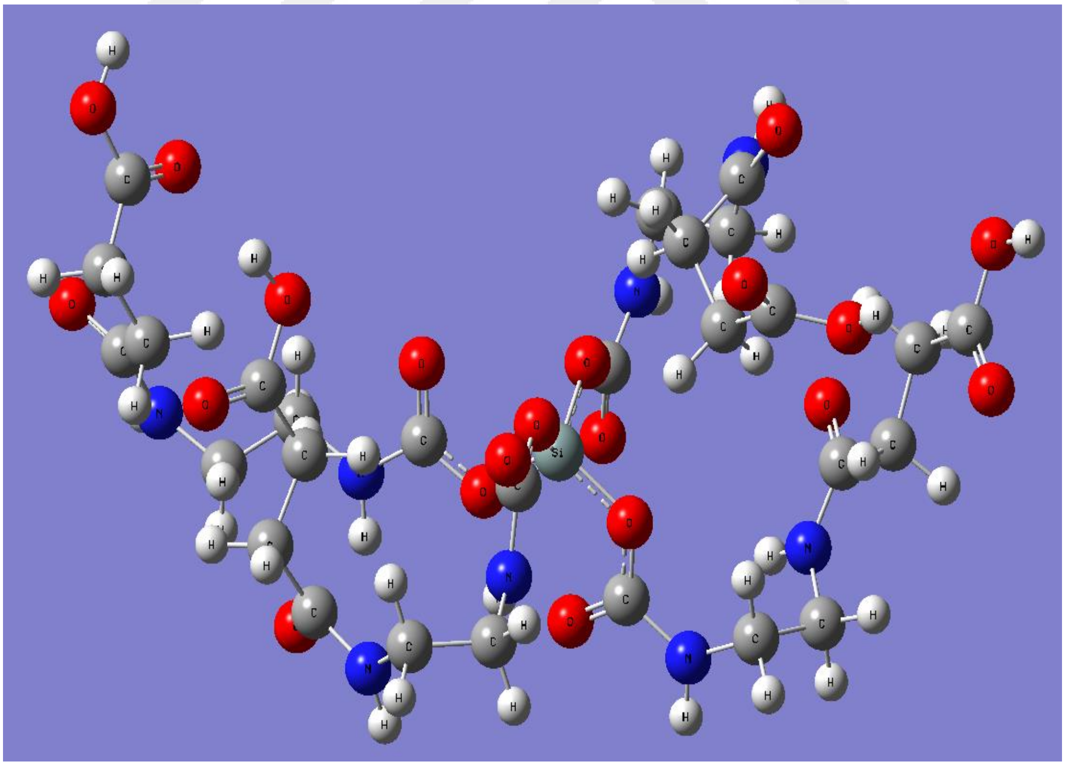

Figure 4.7 Molecular projection of the optimized adsorbent structure which was prepared from rice husk and polyacrylamide (rha-pa).

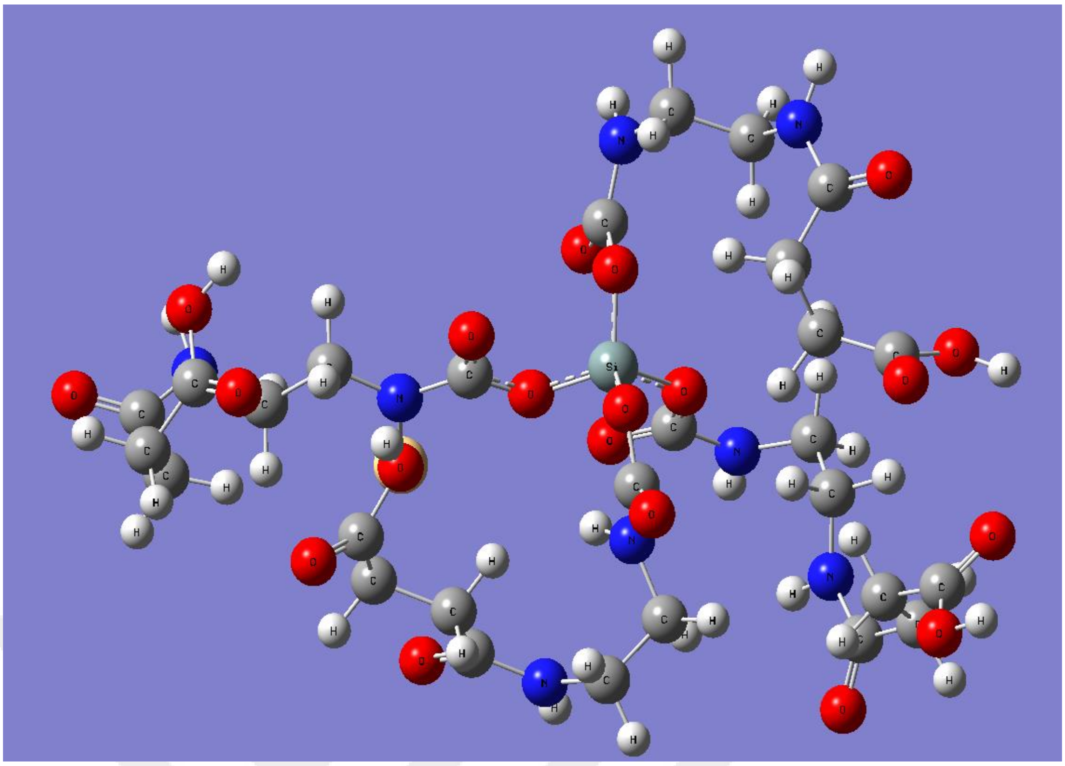

Figure 4.8 Molecular projection of the optimized rha-pa-cd-N1(3) structure.

4.2. Results of Adsorption Simulation

According to studies of Sharma and friends polymer grafted rice husk is an effective and cost effective adsorbent for adsorption of Cd^{2+} ions from aqueous medium. 85% of Cd^{2+} ions can be removed in the optimum conditions which is; pH 9 in 3 h in the concentration range 30–300 mg/L. In recent studies adsorption capacity of rice husk is determined as 21.36 mg/g according to study of Roy et al. (1993) , Munaf and Zein (1997) calculated 0.16 mg/g , and in the study of Tarley et al. adsorption capacity of rice husk is 4 mg/g when unmodified and 7 mg/g when modified with NaOH solution (Chuach et al., 2005).

In our study we used a computer programming to show the adsorbative feature of rice husk. Adsorption energies of Cd^{2+} bounded configurations have been calculated. The following table shows the adsorption energy of geometrically optimized possible structures after Cd^{2+} ion bonded. In graphics adsorption energies in the state of single, double, quad or six binding of Cd^{2+} ion are evaluated among themselves. Results shows us that adsorption energy of rice husk is 24.976 before being treated with polymer and 82.4124 after being treated with polymer. This result indicates that adsorption capacity of rice husk is increasing with polymer treatment.

Table 4.2. Adsorption energies of rice husk, polyacrylamide, adsorbent, and Cd^{2+} bounded configurations.

Structures	Adsorption Energy (kcal/mol)	Structures	Adsorption Energy (kcal/mol)
rha-pa	82.4124	rha-pa-cd-N2(4)	87.4605
rha-pa-cd-O1(1)	86.0835	rha-pa-cd-N2(5)	66.1797
rha-pa-cd-O1(2)	83.3489	rha-pa-cd-N2(6)	61.4675
rha-pa-cd-O1(3)	83.0623	rha-pa-cd-N2(7)	91.3437
rha-pa-cd-O1(4)	84.5965	rha-pa-cd-N2(8)	83.7239
rah-pa-cd-N1(1)	63.5832	rha-pa-cd-N2(9)	166.2839
rha-pa-cd-N1(2)	83.5797	rha-pa-cd-N2(10)	86.3204
rha-pa-cd-N1(3)	86.3247	rha-pa-cd-N2(11)	83.8508
rha-pa-cd-N1(4)	84.9229	rha-pa-cd-N2(12)	86.6189
rha-pa-cd-N1(5)	86.2677	rha-pa-cd-N4(1)	66.303
rha-pa-cd-N1(6)	86.4993	rha-pa-cd-N4(2)	85.4666
rha-pa-cd-N1(7)	85.058	rha-pa-cd-N4(3)	172.7259
rha-pa-cd-N1(8)	85.1094	rha-pa-cd-N4(4)	83.6987
rha-pa-cd-O2(1)	84.353	rha-pa-cd-N4-O2(1)	67.2506
rha-pa-cd-O2(2)	83.5686	rha-pa-cd-N4-O2(2)	91.3294
rha-pa-cd-O2(3)	83.1906	rha-pa-cd-N4-O2(3)	65.5552
rha-pa-cd-O2(4)	91.1416	rha-pa-cd-N4-O2(4)	79.8491
rha-pa-cd-N2(1)	63.9042	pa-cis	17.3024
rha-pa-cd-N2(2)	86.2577	pa-trans	17.7942
rha-pa-cd-N2(3)	86.998	Rha	24.976

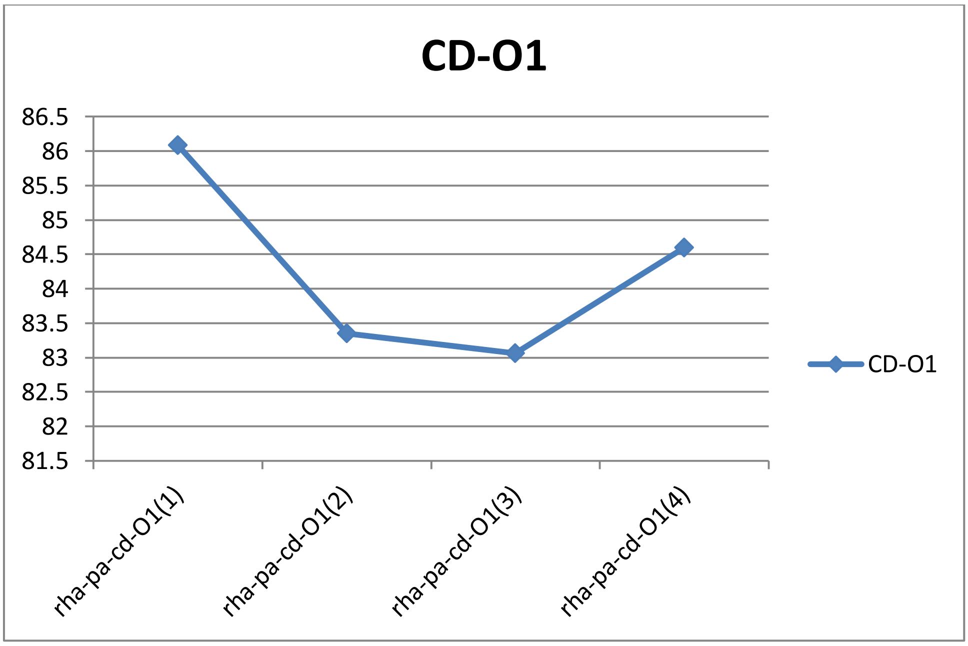

Figure 4.9 Adsorption energies of structures when Cd^{2+} ion has a single bond with four O atoms.

The adsorption energies when Cd^{2+} ion has a single bond with different four O atoms are very close to each other, but it is seen that the adsorption energy of rha-pa-cd-O1(1) is higher. Higher adsorption energy shows that structure is less stable and has a higher adsorption capacity.

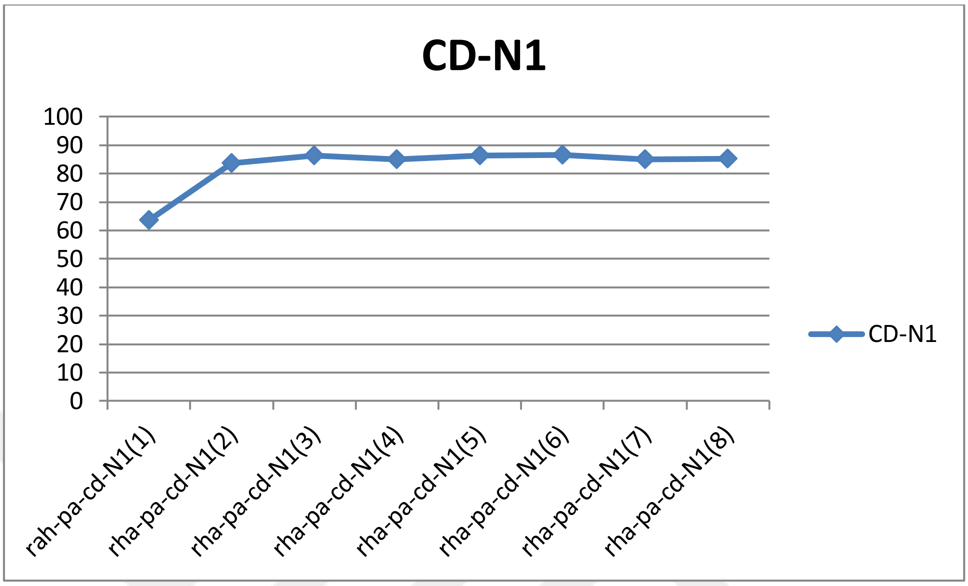

Figure 4.10 Adsorption energies of structures when Cd^{2+} ion has a single bond with N atoms.

When the eight situations where Cd^{2+} ion binds to N with a single bond, it is seen that rha-pa-cd-N1(6) structure has a higher adsorption capacity.

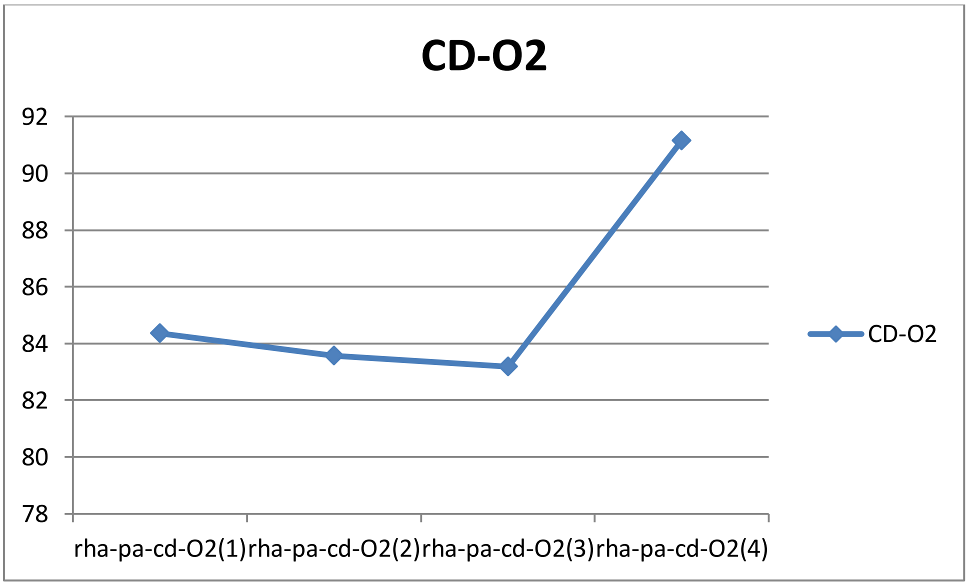

Figure 4.11 Adsorption energies of structures when Cd^{2+} ion has a double bond with O atom.

When double bonds with O are considered, the rha-pa-cd-O2(4) structure has a higher adsorption capacity.

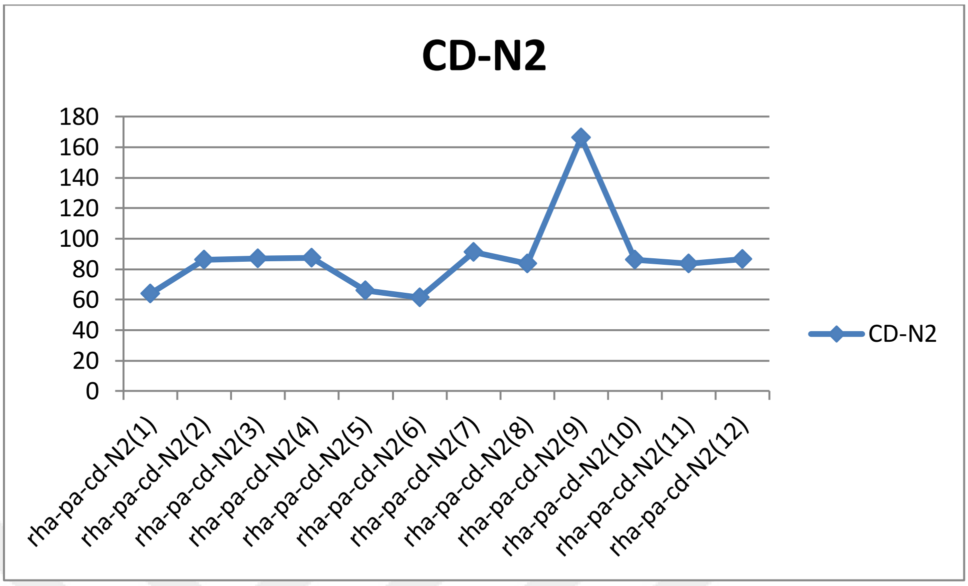

Figure 4.12 Adsorption energies of structures when Cd^{2+} ion has a double bond with N atom.

In the same manner, when the twelve situations where the Cd^{2+} bond had a double bond with N, the rha-pa-cd-N2 (9) structure has a higher adsorption capacity.

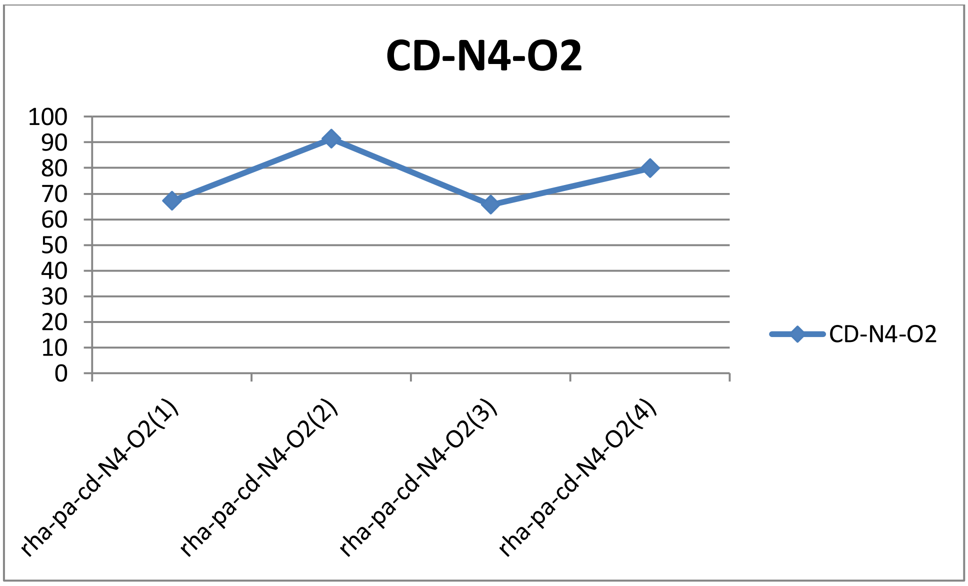

Figure 4.13 Adsorption energies of structures when Cd^{2+} ion has sextant bonds.

In the situations where the Cd^{2+} ion has sextant bonds, the rha-pa-cd-N4-O2 (2) has the highest adsorption capacity.

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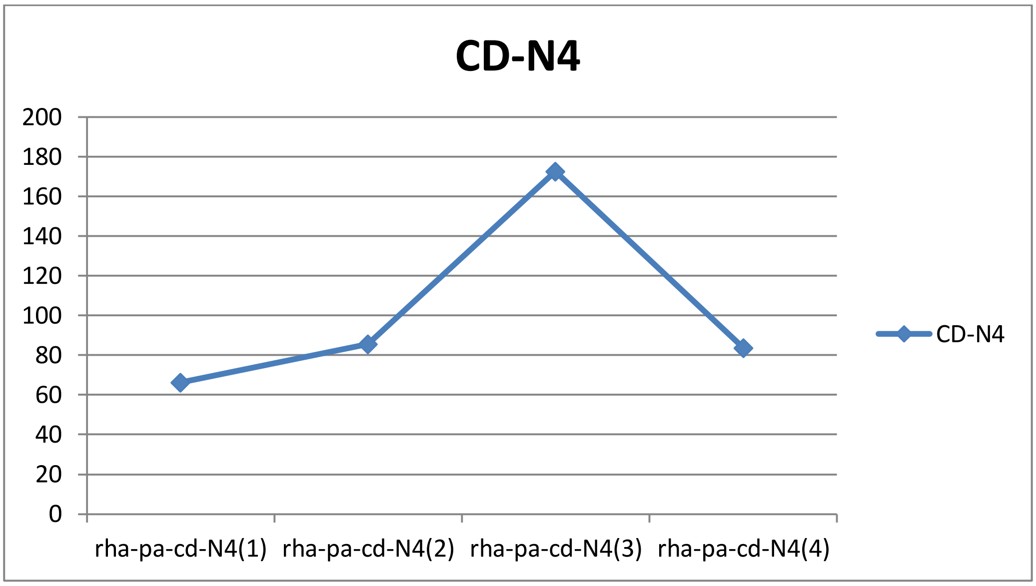

Figure 4.14 Adsorption energies of structures when Cd ion has quadruple bonds

In the quadruple bonds, the rha-pa-cd-N4(3) structure has the highest adsorption energy.

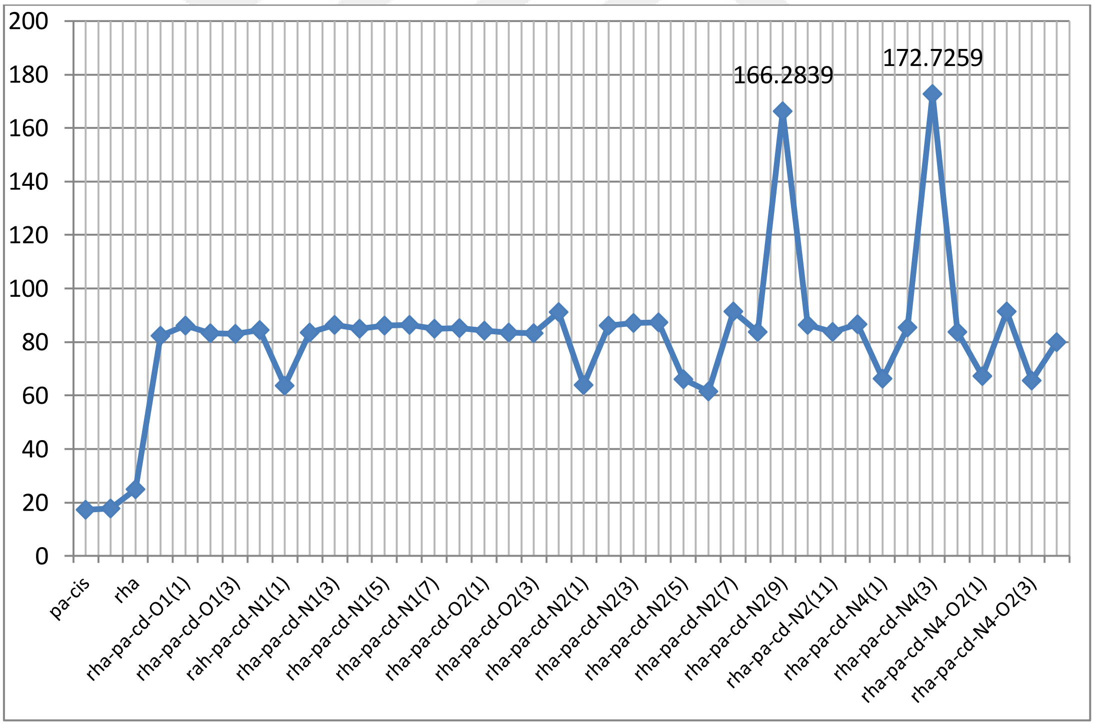

Figure 4.15 Adsorption energies of all possible structures.

When all of the structures are considered, the highest adsorption capacity belongs to the rha-pa-cd- N4(3) structure.

4.3. Discussion

In our study, we examined the adsorptive feature of rice husk. Sharma and friends said as a result of their study polymer grafted rice husk is a cost effective adsorbents for adsorption of Cd^{2+} ions from aqueous medium. In recent studies adsorption capacity of rice husk is ; 21.36 mg/g according to study of Roy et al. (1993) , Munaf and Zein (1997) calculated 0.16 mg/g , and in the study of Tarley et al. adsorption capacity of rice husk is 4 mg/g when unmodified and 7 mg/g if modified with NaOH solution (116). Differences from these studies we used a computer programming to show the adsorptive feature of rice husk in our study.

Adsorption energies of Cd^{2+} bounded configurations has been calculated with Material Studio package program. Adsorption energies in the state of single, double, quad or six binding of Cd^{2+} ion are evaluated among themselves. Among all of the structures highest adsorption capacity belongs to the rha-pa-cd- N4(3) structure. Results shows us that adsorption energy of rice husk is 24.976 before being treated with polymer and 82.4124 after being treated with polymer. This result indicates that adsorption capacity of rice husk is increasing with polymer treatment.

CHAPTER 5

5. CONCLUSION

The use of rice husks for adsorption purposes provides a solution to the two big problems, first one is rice husk storage issues due to high production rates, and secondly, it is a cheaper solution to removing heavy metals from industrial wastewater.

In our study, a computer-based approach is proposed to optimize binding mechanism of rice husk by using geometry optimization and adsorption simulation methods. Here the rice husk's adsorption mechanism of Cd^{2+} from industrial wastewater was examined.

The molecular projection of the rice husk, polyacrylamide, the combined structure of them and the probable structures that will occur after Cd^{2+} is adsorbed in the medium were drawn and optimized. The part where Cd^{2+} binds to the structure was determined. When the optimization energies of them are calculated and compared, it was seen that the structures in which the Cd^{2+} ion makes single bonds has lower optimization energies. In this case, it can be said that the structures in which Cd^{2+} ion takes the H ions from the O and N ions are more stable. We used Gaussian® 09 package software for these geometry optimizations.

The adsorptive features of rice husk were shown by using Material Studio® 6.1 software. Adsorption energies of Cd^{2+} bounded configurations have been calculated and compared. Here, the structure which has the highest energy value was selected. This showed us that rice husks can be used as adsorbents instead of expensive materials such as active carbon. This result indicates that adsorption capacity of rice husk is increasing with polymer treatment. As a conclusion, a computer-based approach was developed by using the obtained results of experimental methods in different studies in literature. It is said that the proposed approach is more quickly and less costly, when compared with experimental methods.

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http://www.tuik.gov.tr/PreTablo.do?alt_id=1001 (Source: Ministry of Agriculture and Livestock), 20.08.2013.

http://www.usda.gov/oce/commodity/wasde/latest.pdf, 20.08.2013.

APPENDIX-A

Figure 1. Molecular projection of rice husk ash (rha)

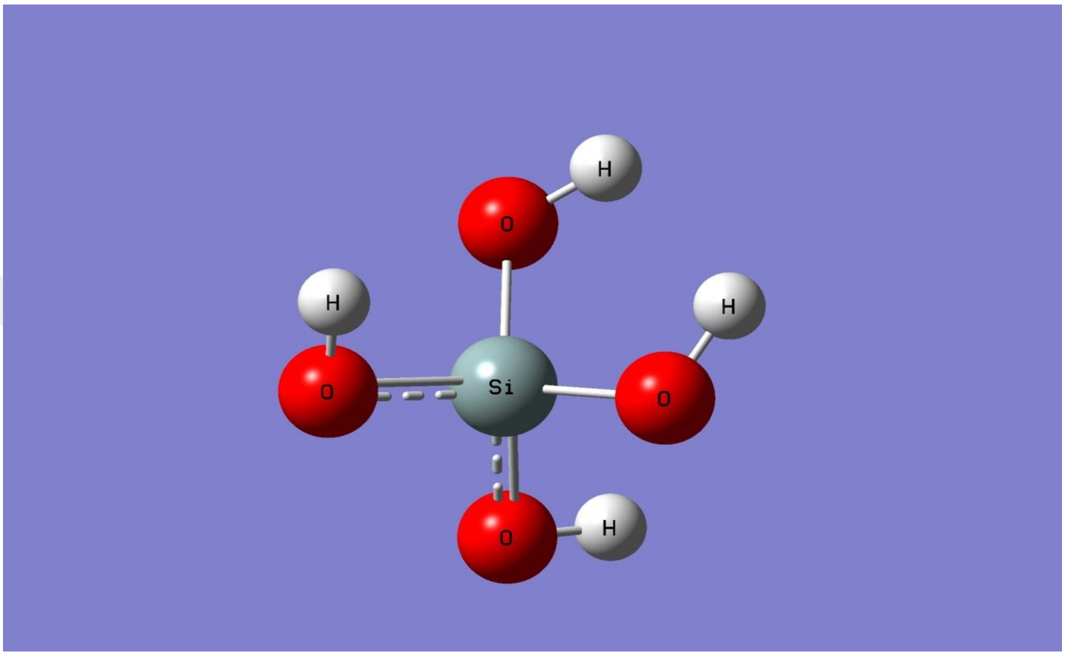

Figure 2. Molecular projection of adsorbent (rha-pa)

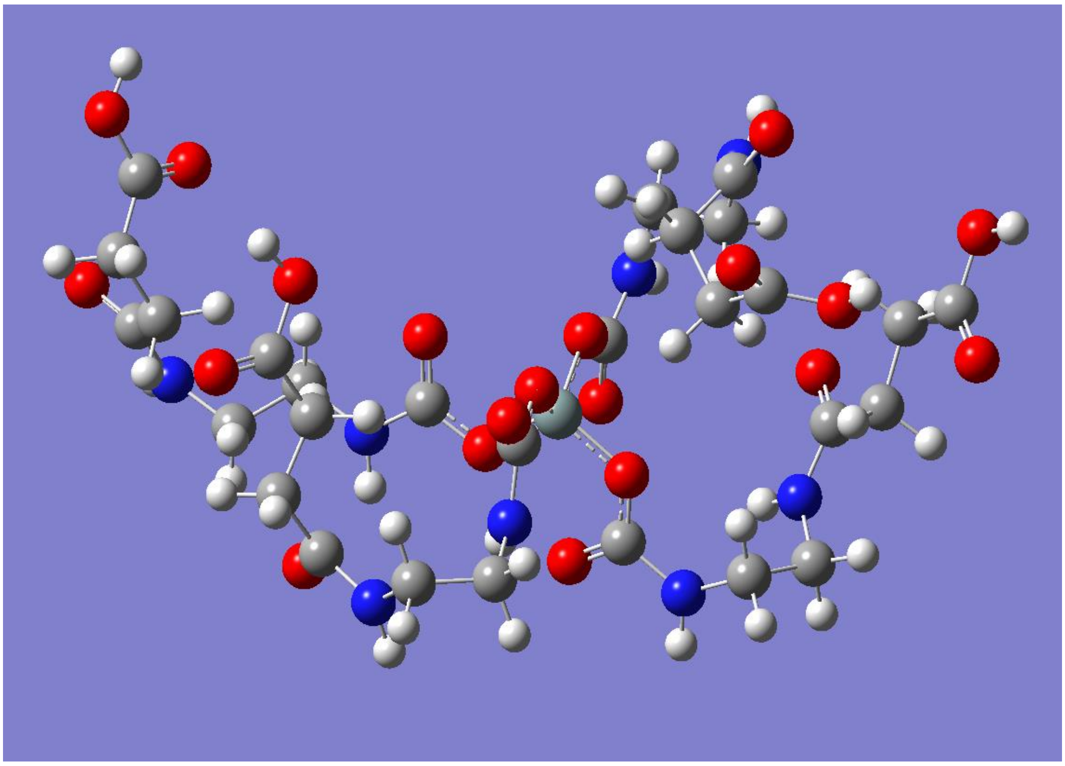

Figure 3. Molecular projection of rha-pa-cd-N1(1)

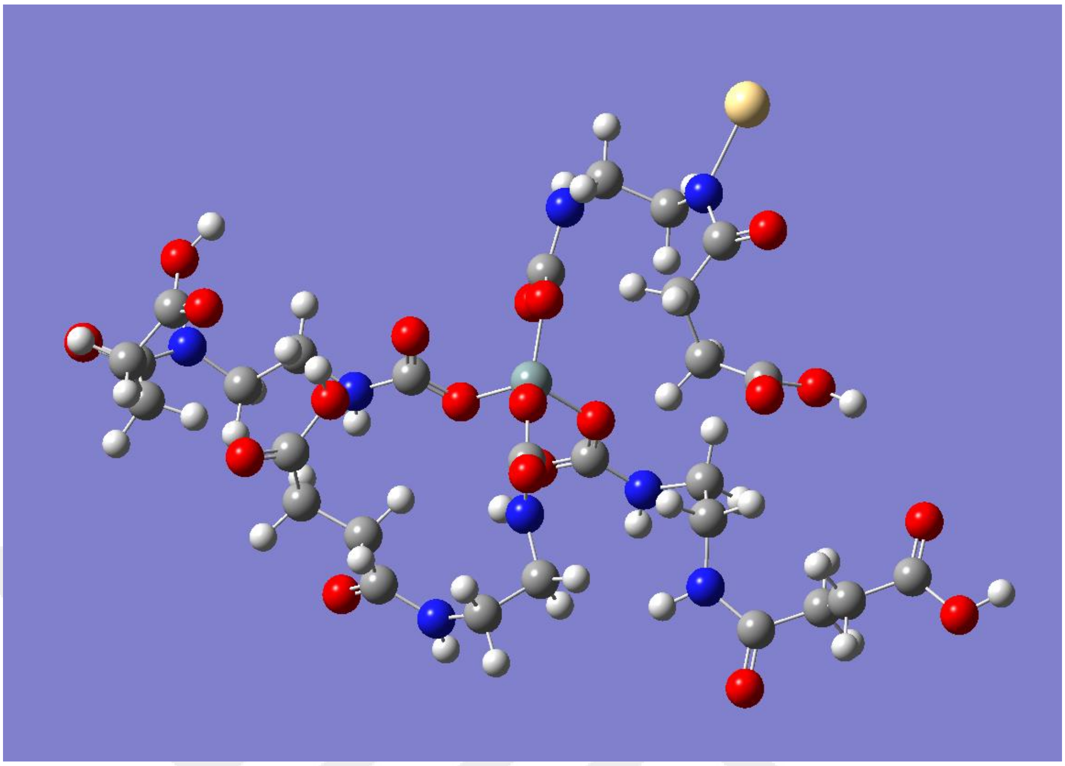

Figure 4. Molecular projection of rha-pa-cd-N1(2)

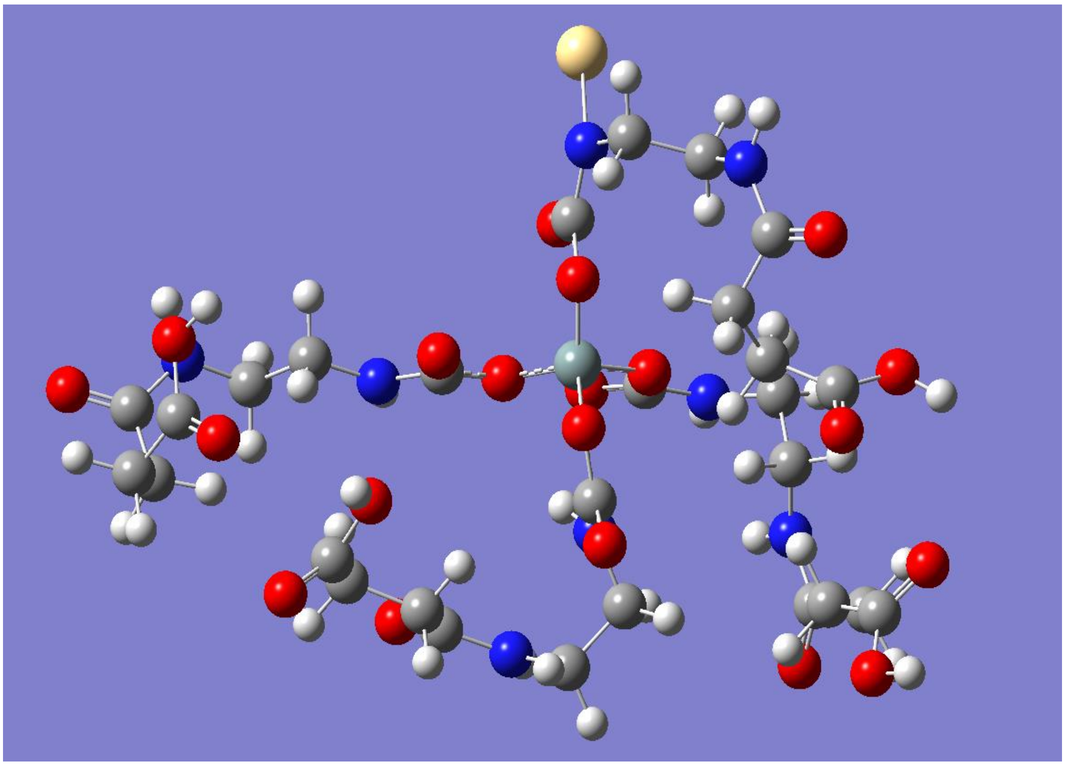

Figure 5. Molecular projection of rha-pa-cd-N1(3)

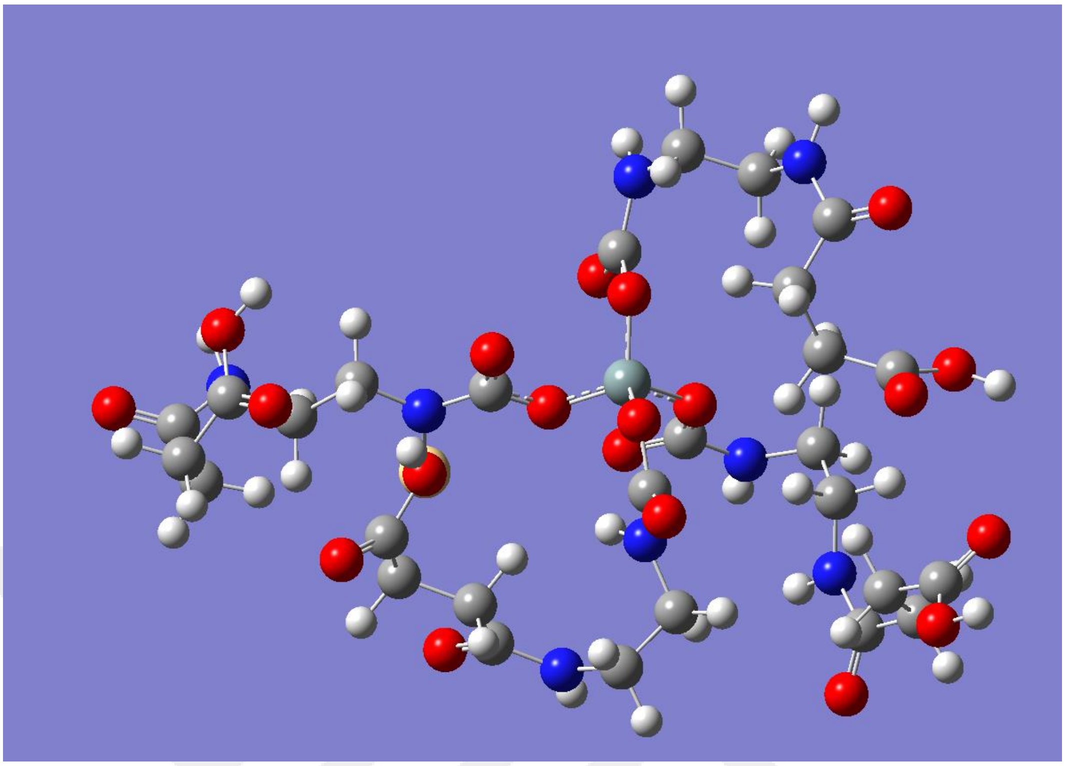

Figure 6. Molecular projection of rha-pa-cd-N1(4)

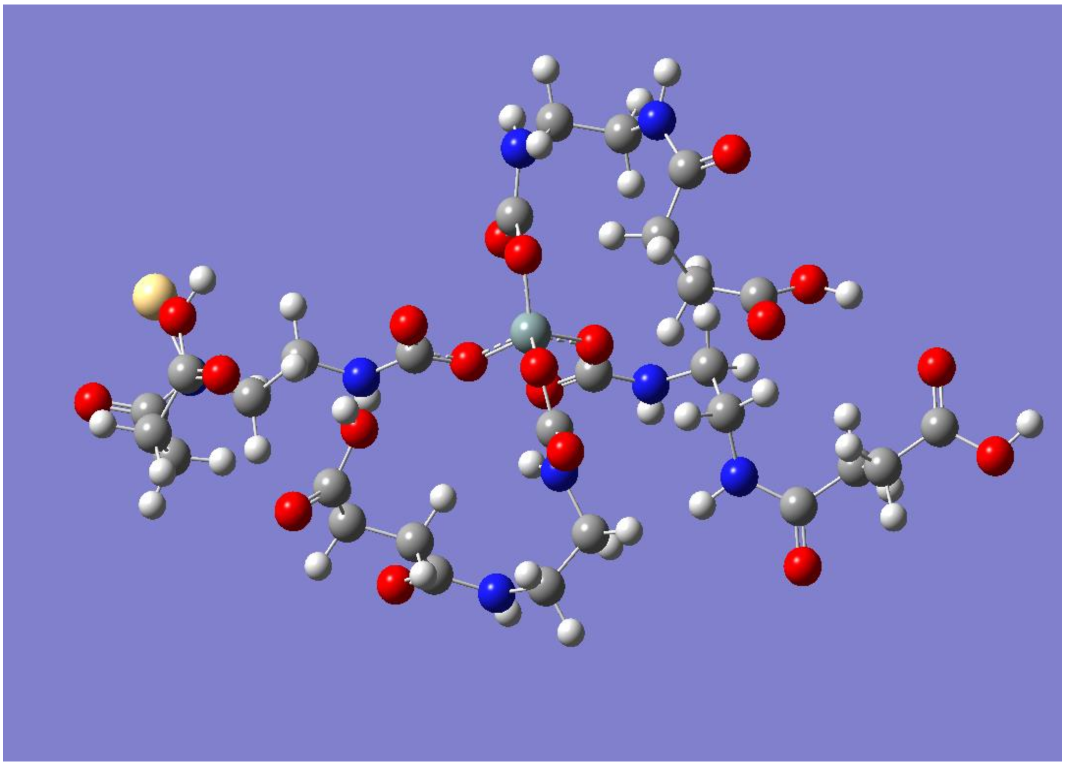

Figure 7. Molecular projection of rha-pa-cd-N1(5)

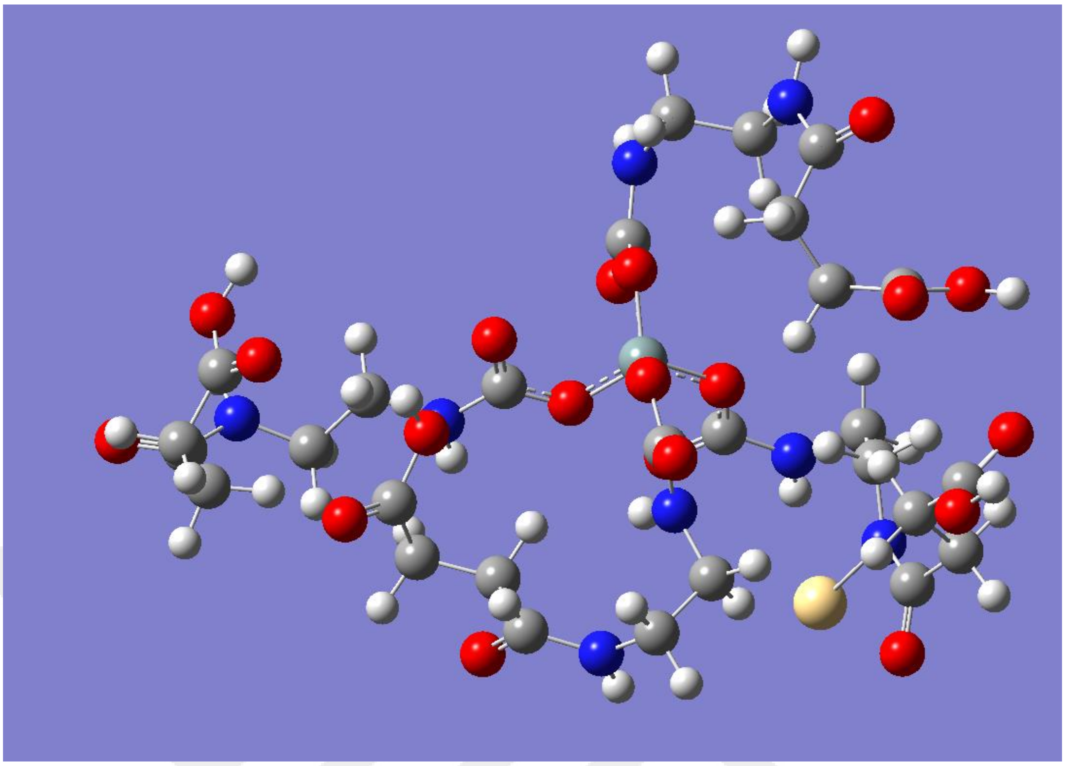

Figure 8. Molecular projection of rha-pa-cd-N1(6)

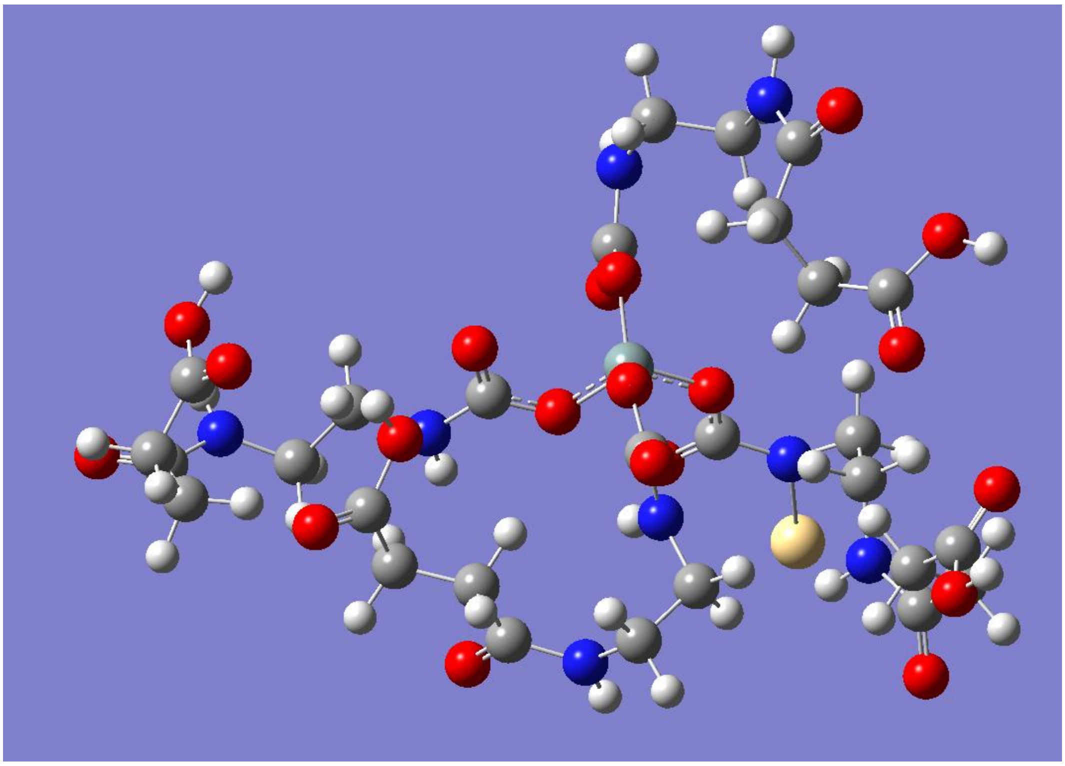

Figure 9. Molecular projection of rha-pa-cd-N1(7)

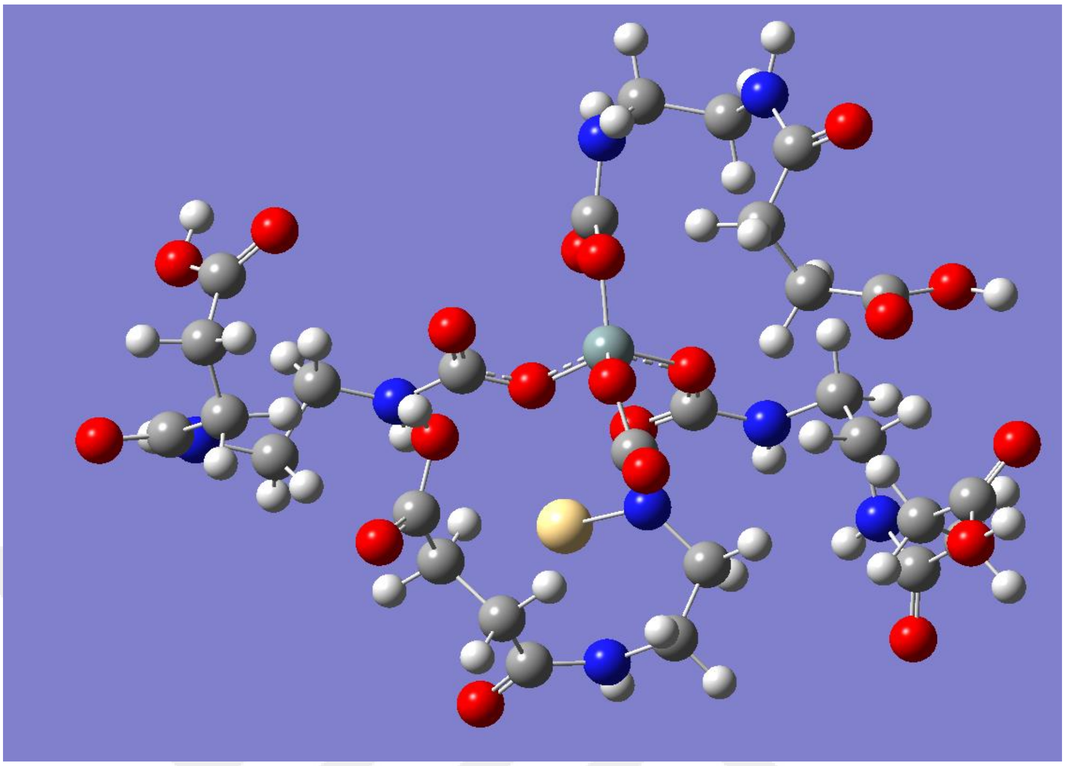

Figure 10. Molecular projection of rha-pa-cd-N1(8)

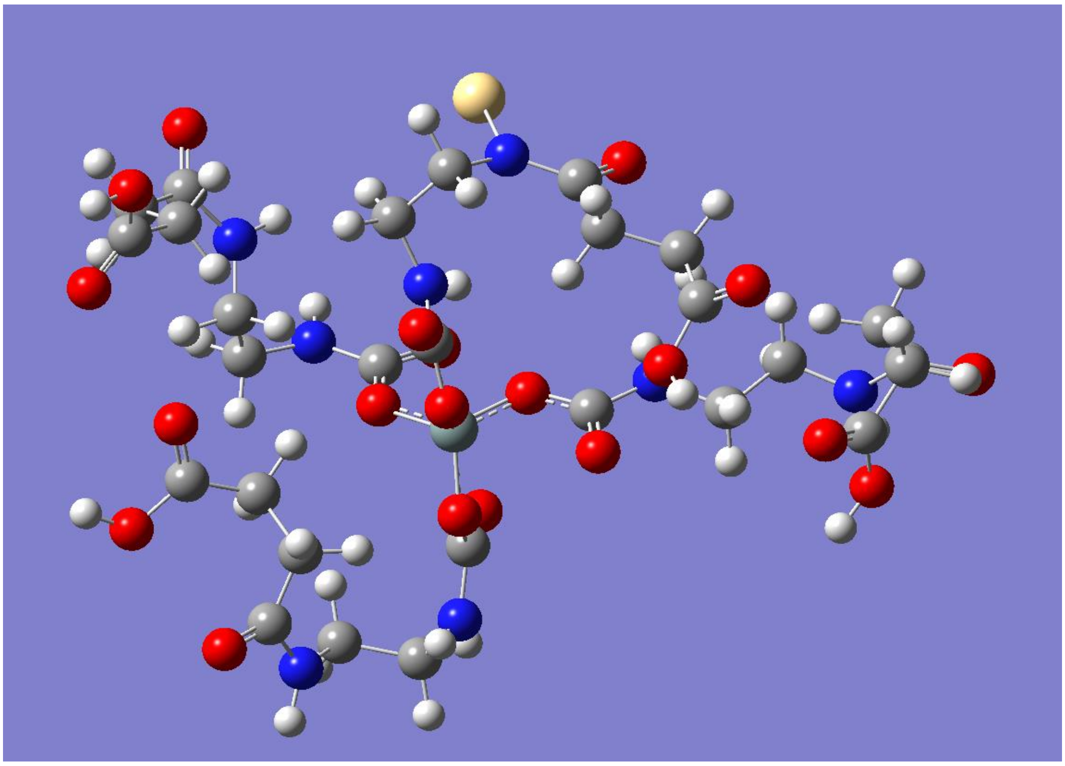

Figure 11. Molecular projection of rha-pa-cd-N2(1)

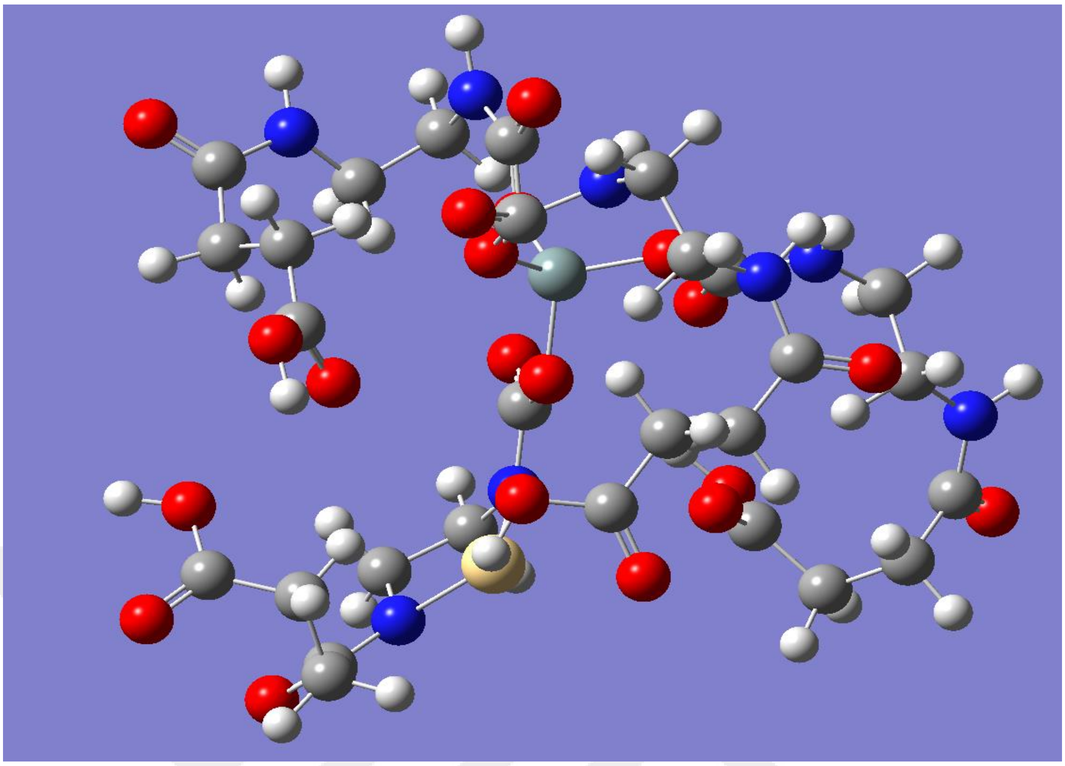

Figure 12. Molecular projection of rha-pa-cd-N2(2)

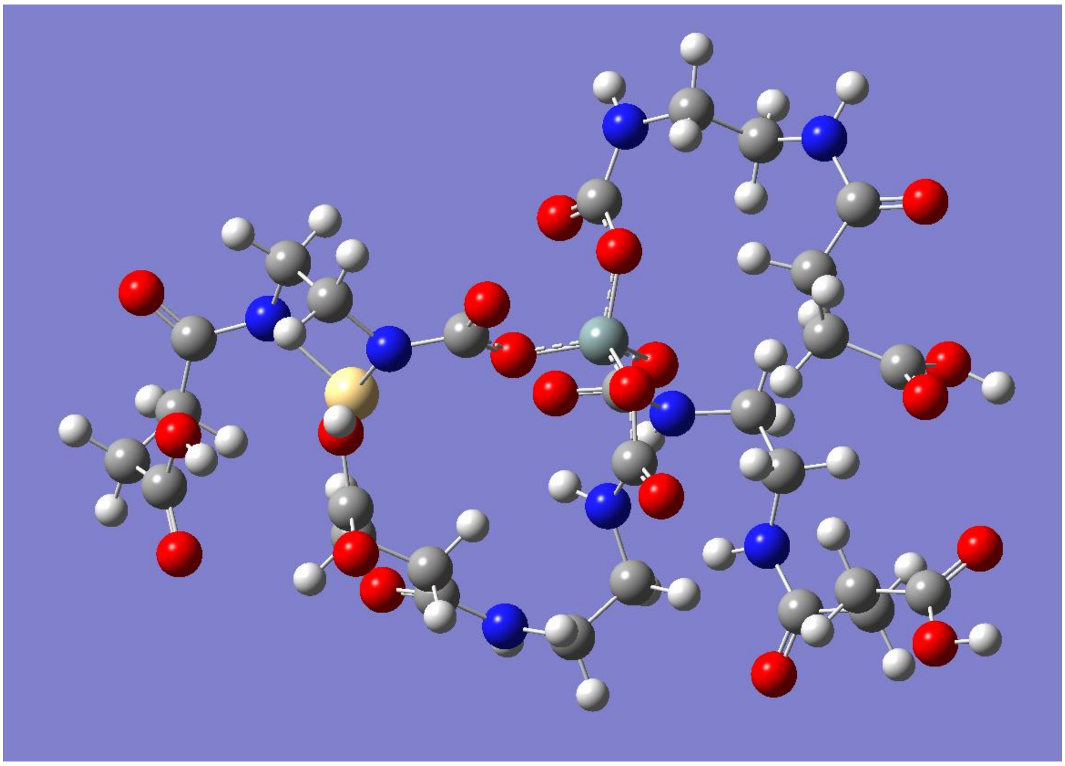

Figure 13. Molecular projection of rha-pa-cd-N2(3)

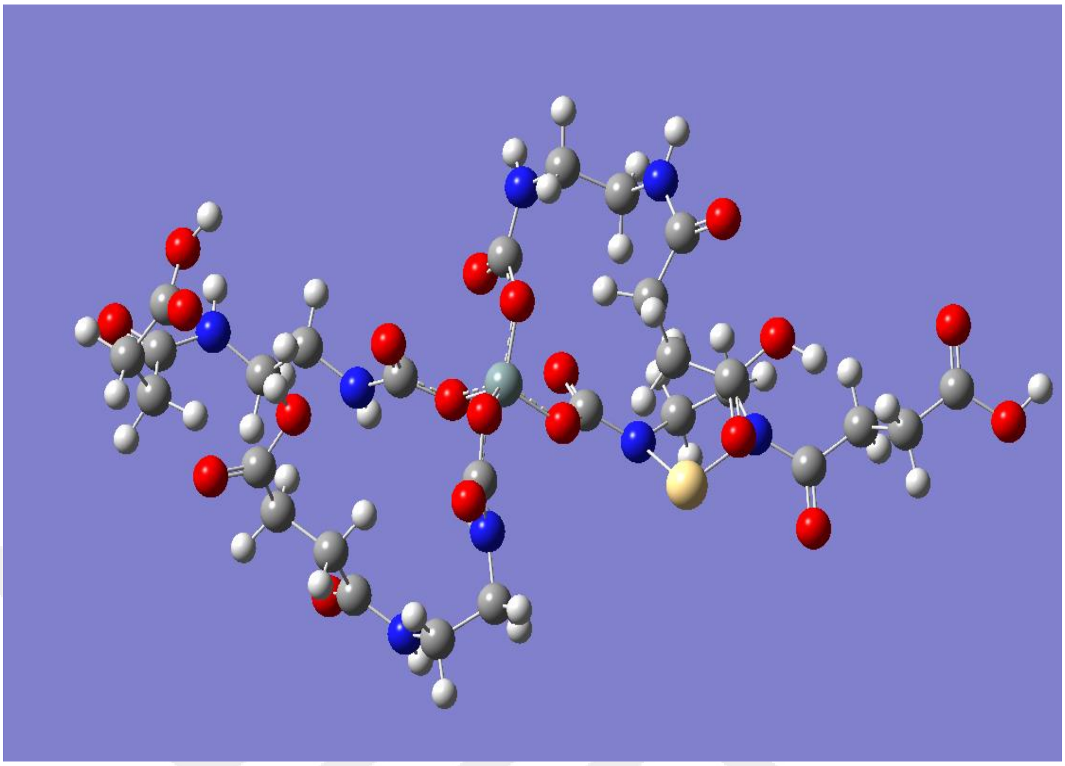

Figure 14. Molecular projection of rha-pa-cd-N2(4)

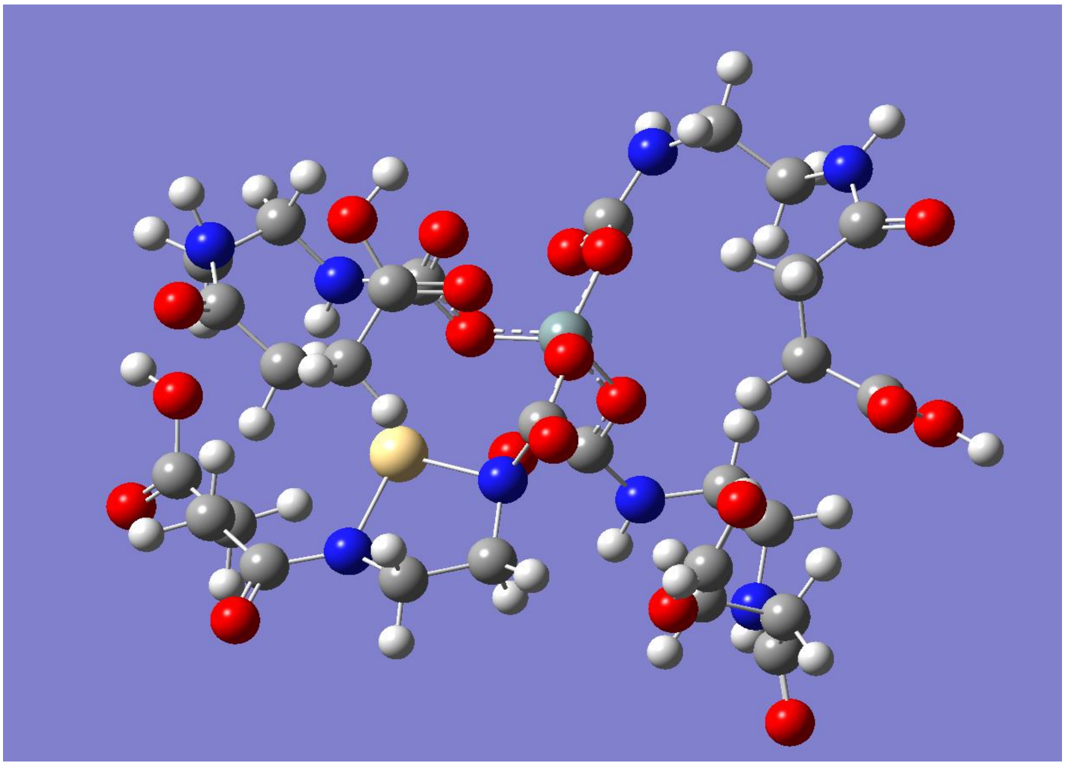

Figure 15. Molecular projection of rha-pa-cd-N2(5)

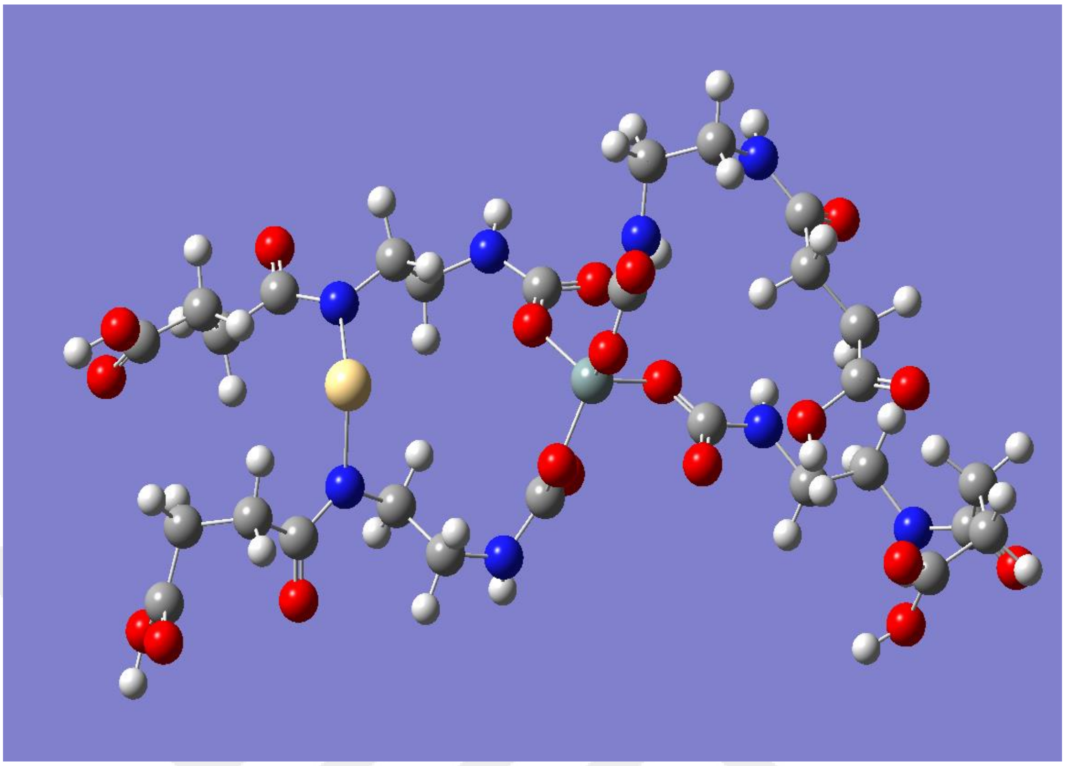

Figure 16. Molecular projection of rha-pa-cd-N2(6)

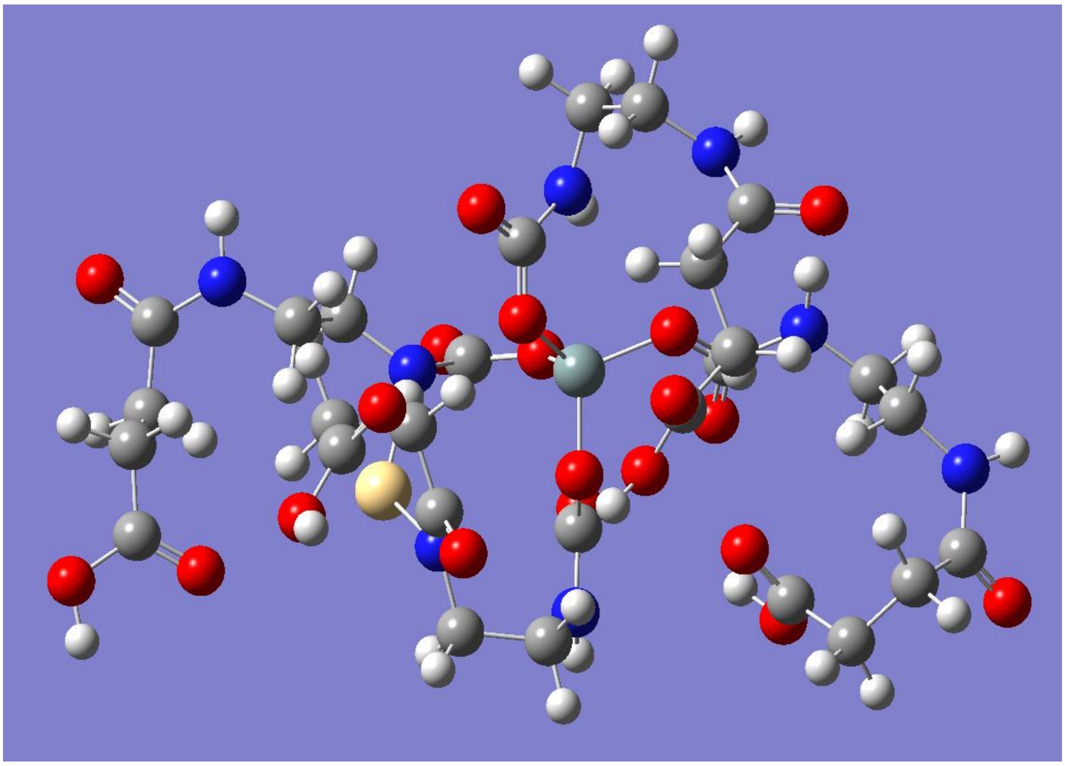

Figure 17. Molecular projection of rha-pa-cd-N2(7)

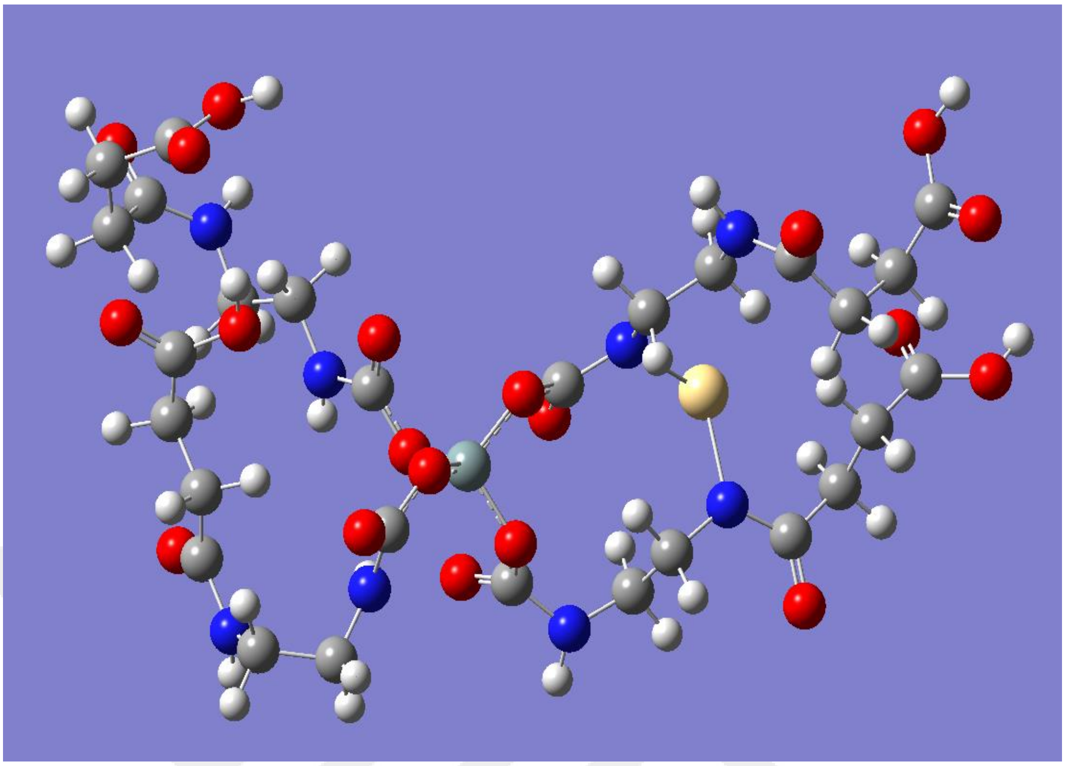

Figure 18. Molecular projection of rha-pa-cd-N2(8)

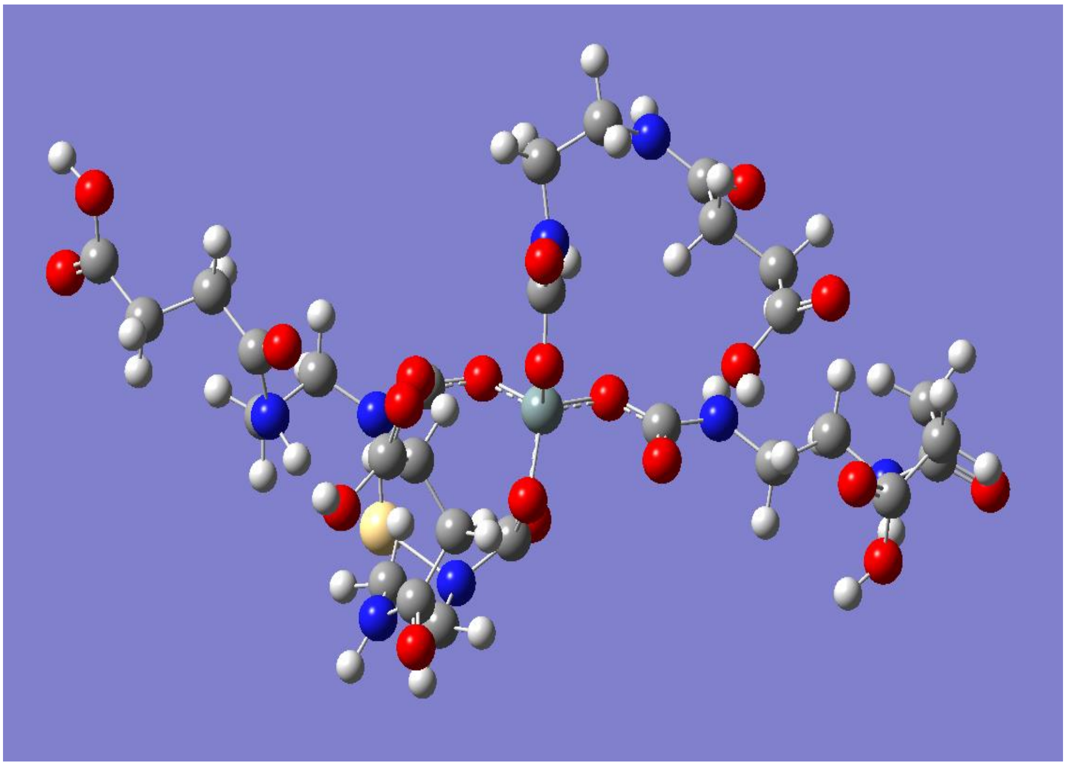

Figure 19. Molecular projection of rha-pa-cd-N2(9)

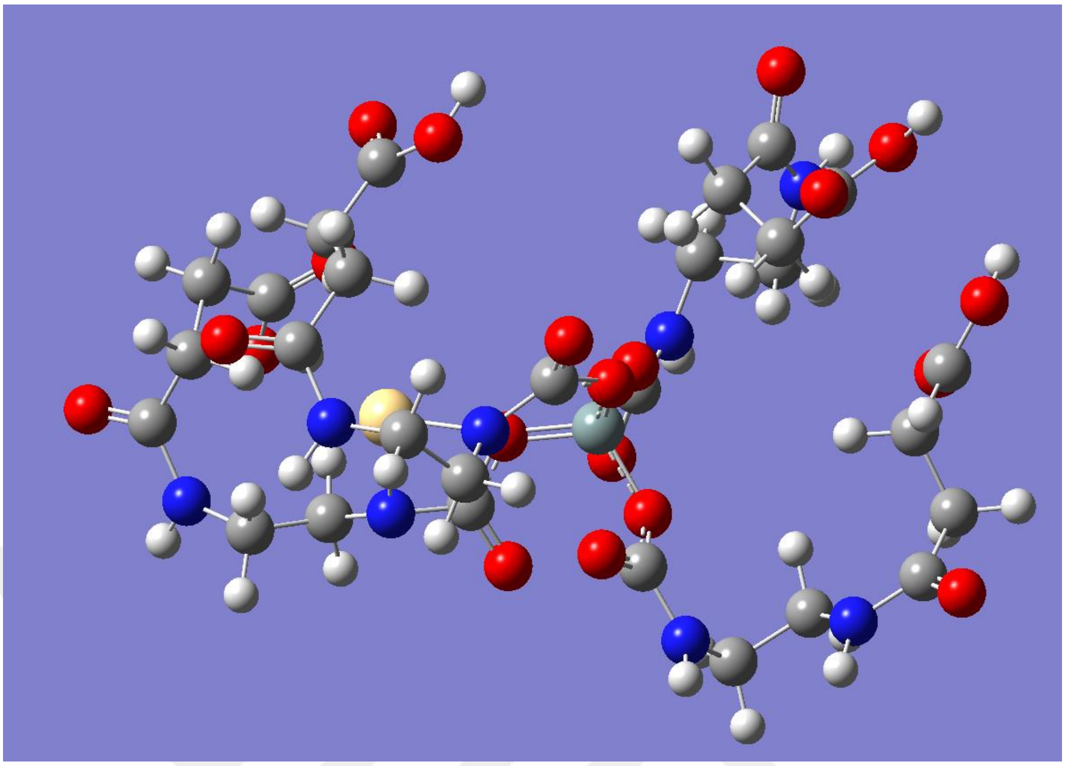

Figure 20. Molecular projection of rha-pa-cd-N2(10)

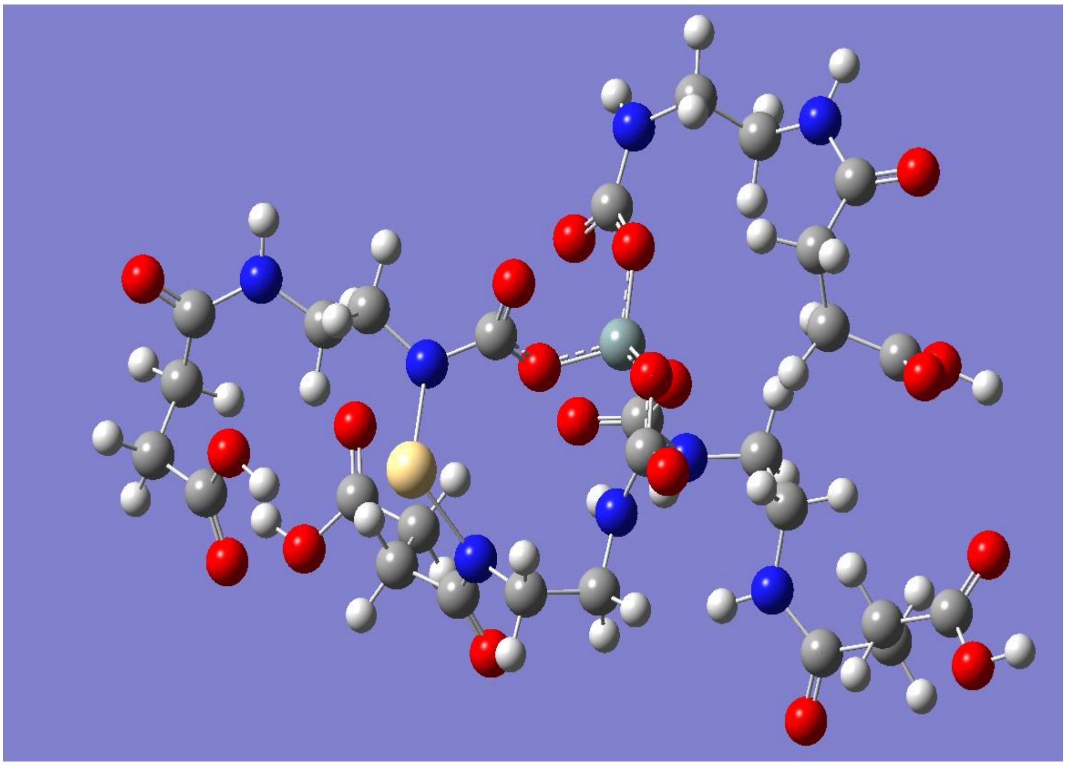

Figure 21. Molecular projection of rha-pa-cd-N2(11)

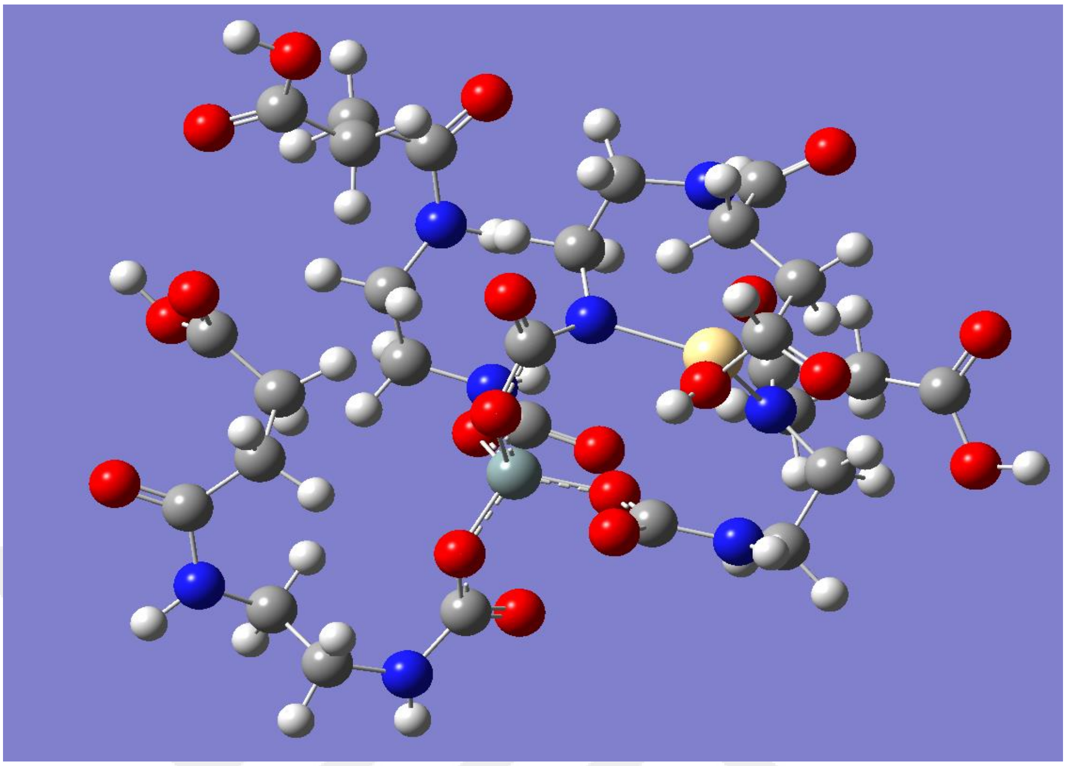

Figure 22. Molecular projection of rha-pa-cd-N2(12)

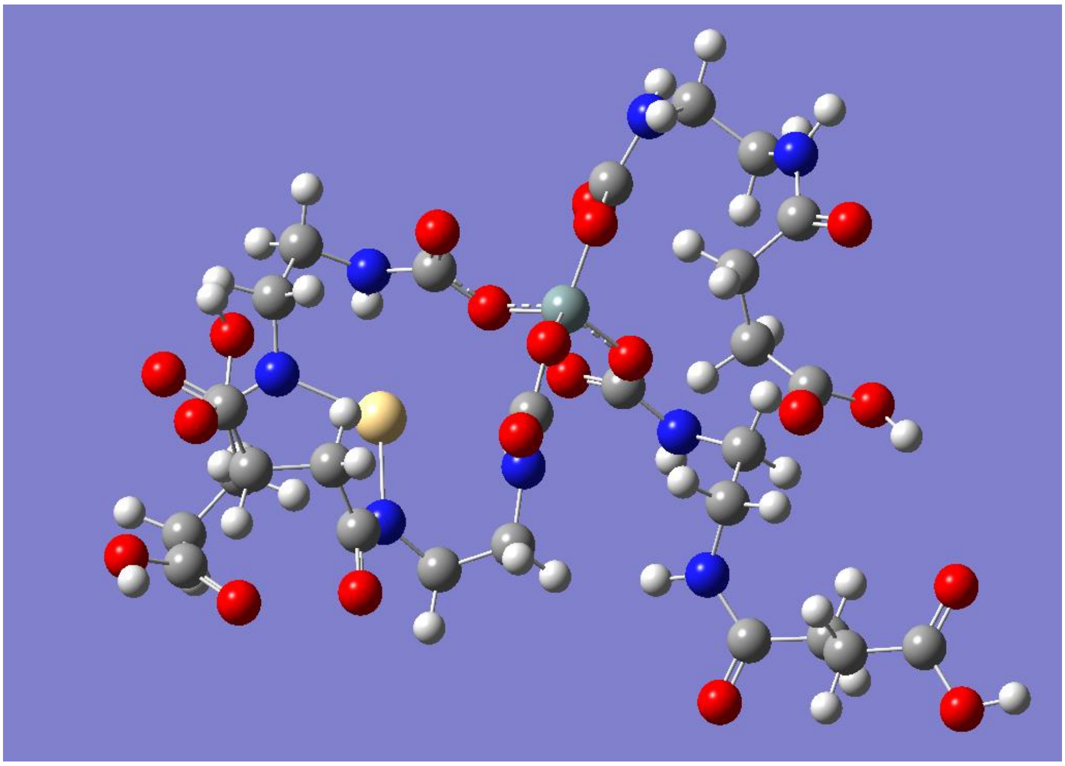

Figure 23. Molecular projection of rha-pa-cd-N4(1)

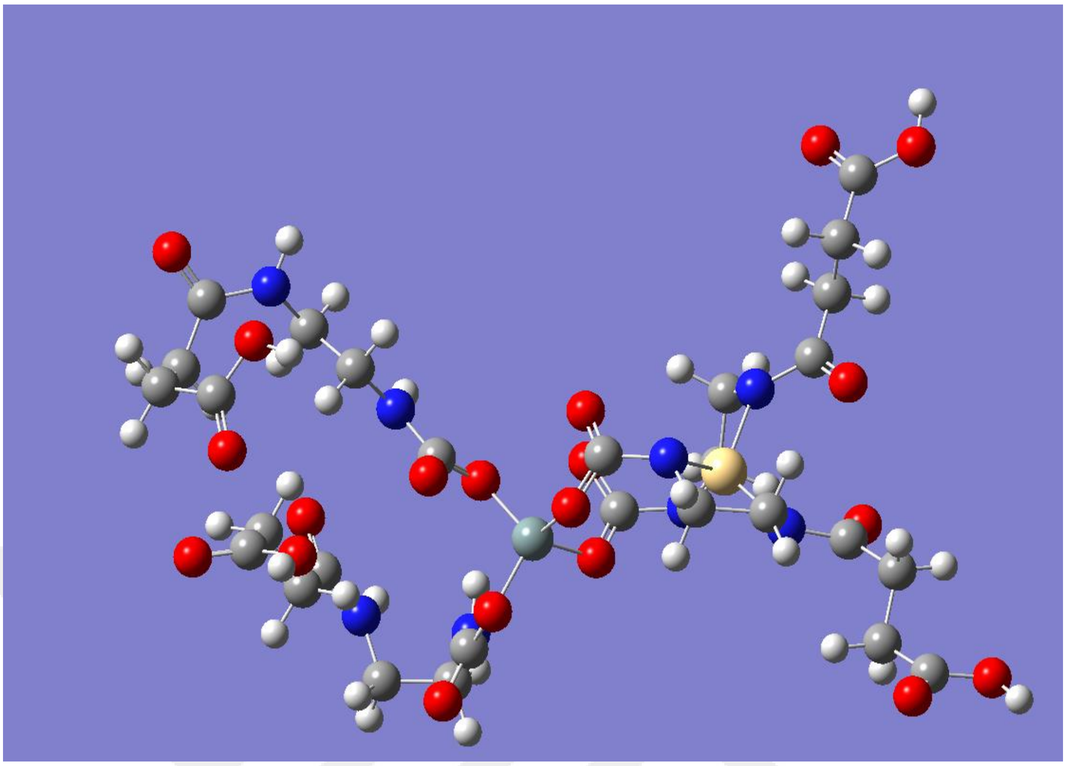

Figure 24. Molecular projection of rha-pa-cd-N4(2)

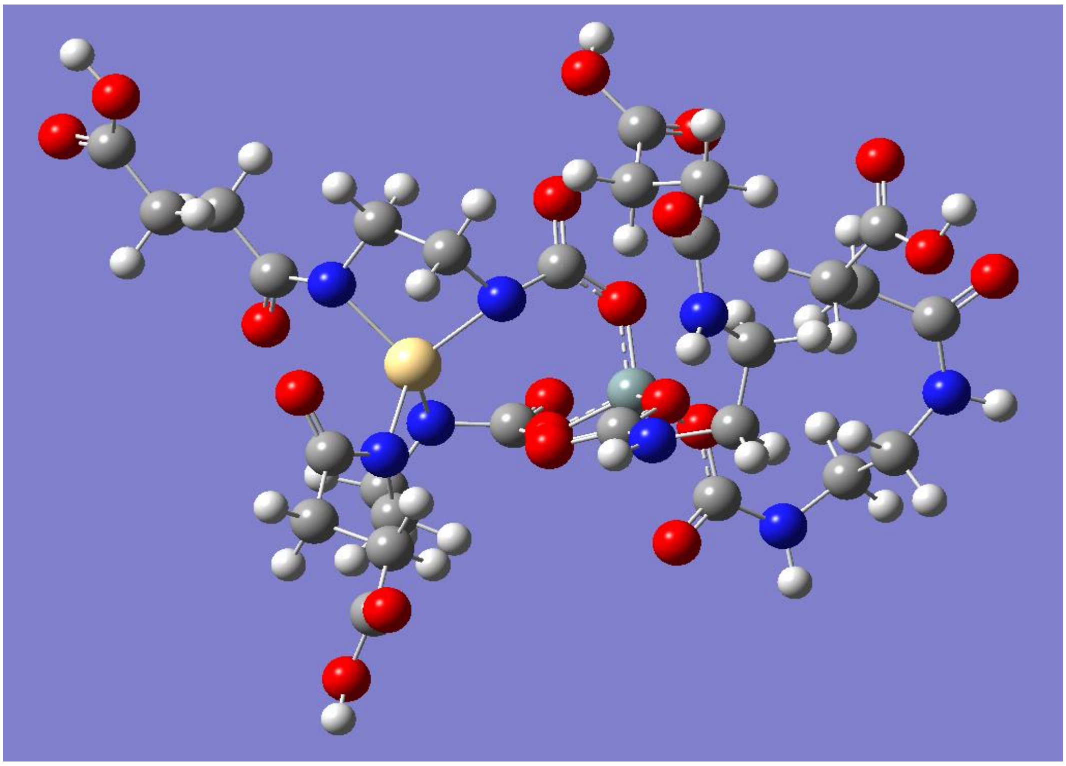

Figure 25. Molecular projection of rha-pa-cd-N4(3)

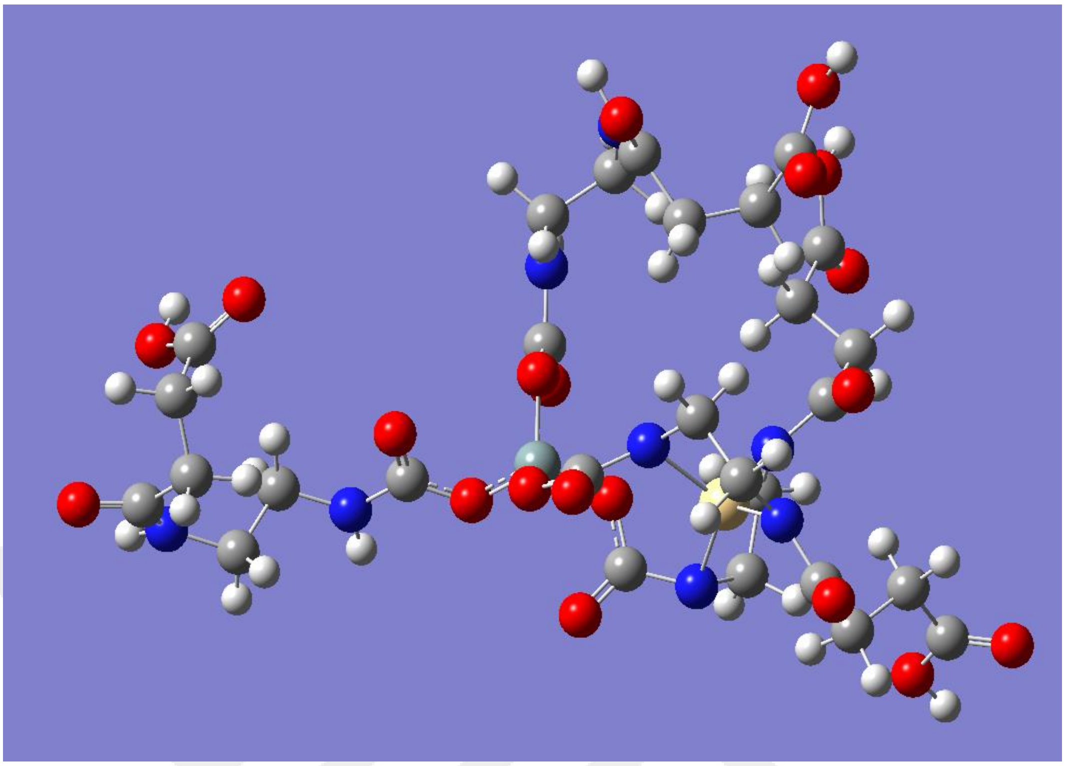

Figure 26. Molecular projection of rha-pa-cd-N4(4)

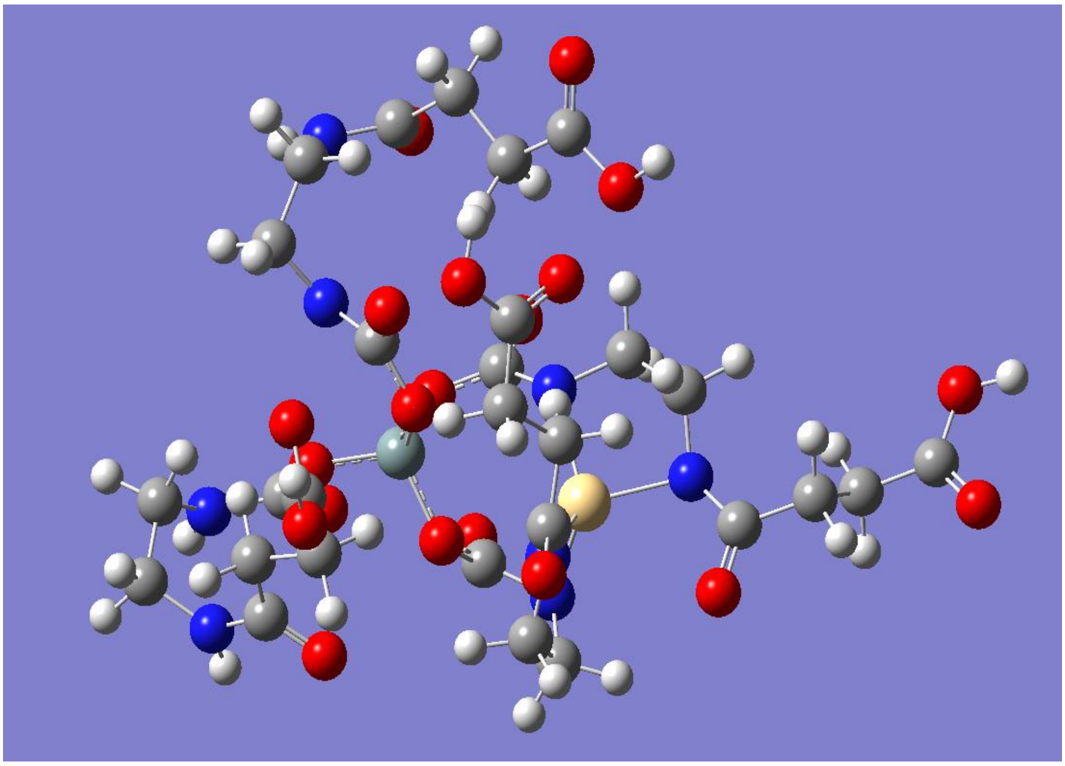

Figure 27. Molecular projection of rha-pa-cd-N4-O2(1)

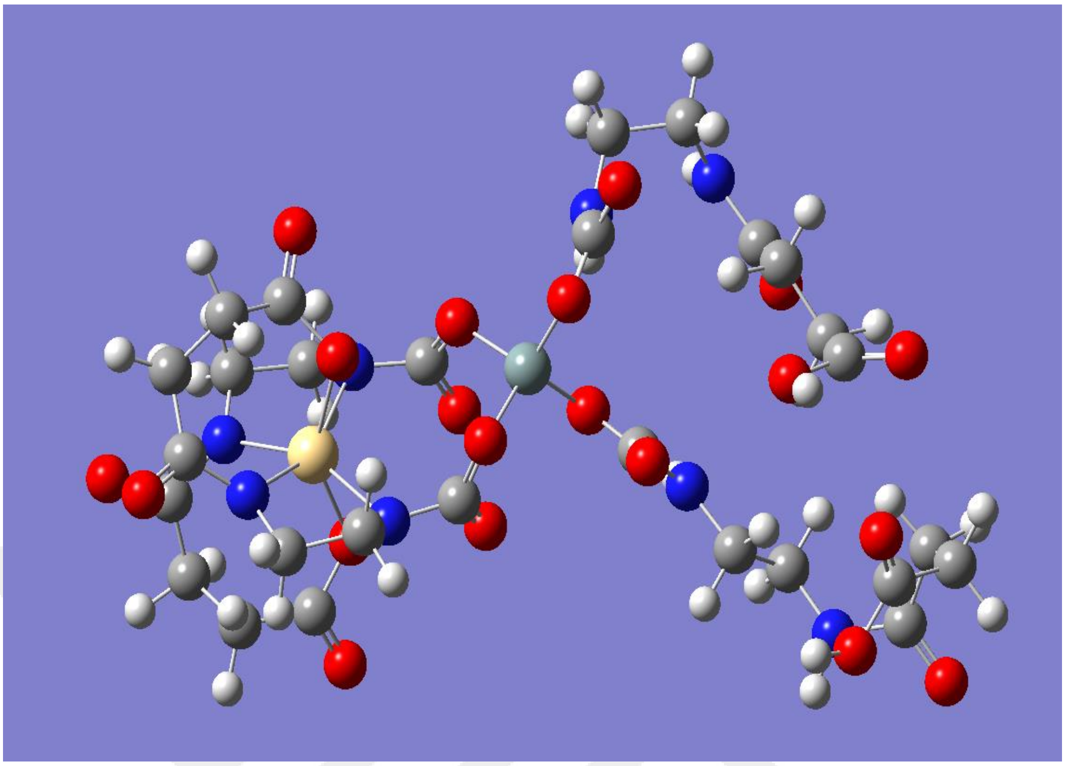

Figure 28. Molecular projection of rha-pa-cd-N4-O2(2)

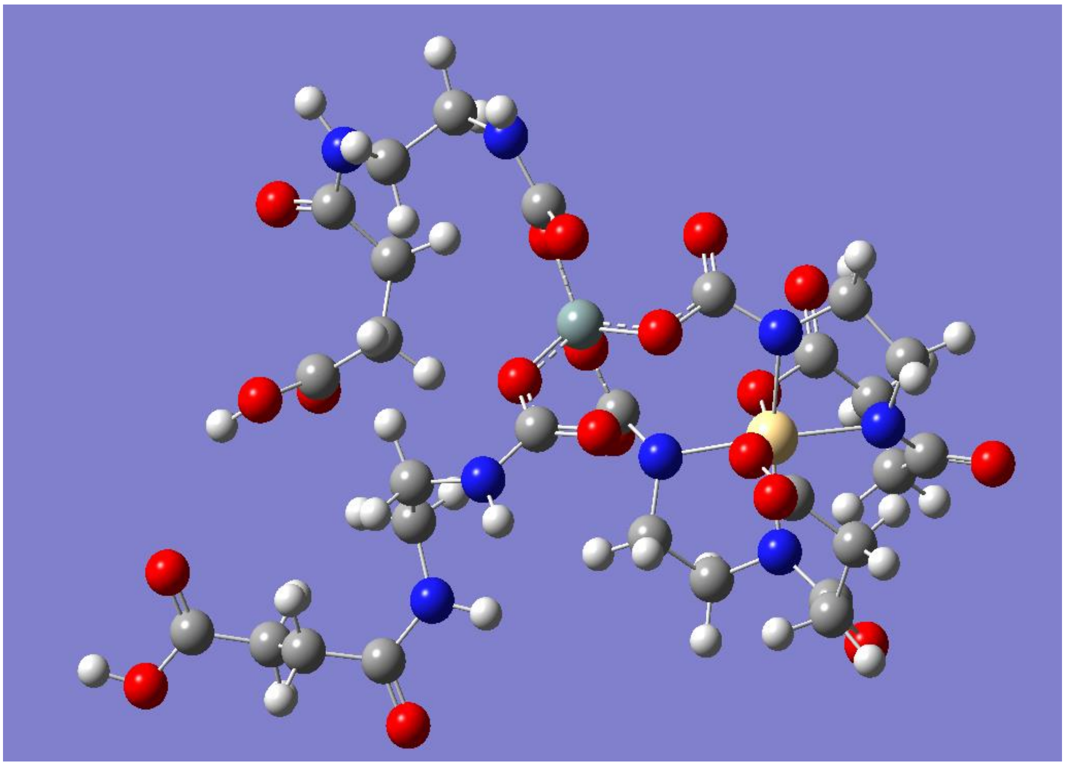

Figure 29. Molecular projection of rha-pa-cd-N4-O2(3)

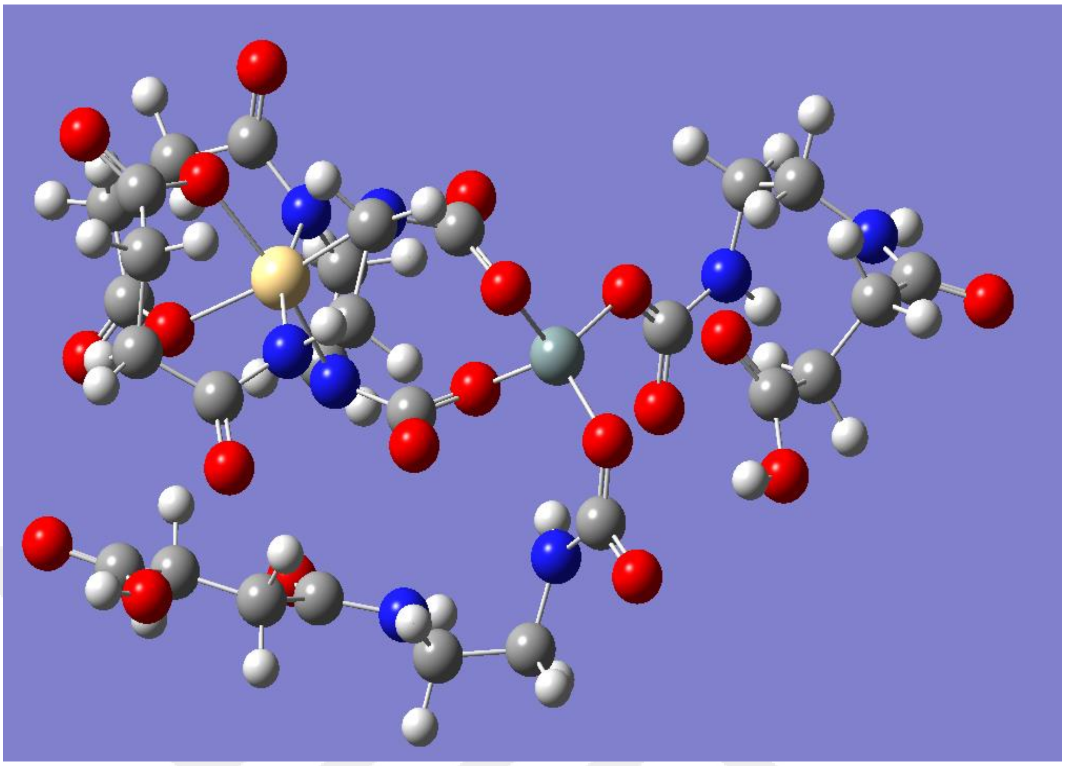

Figure 30. Molecular projection of rha-pa-cd-N2-O2(4)

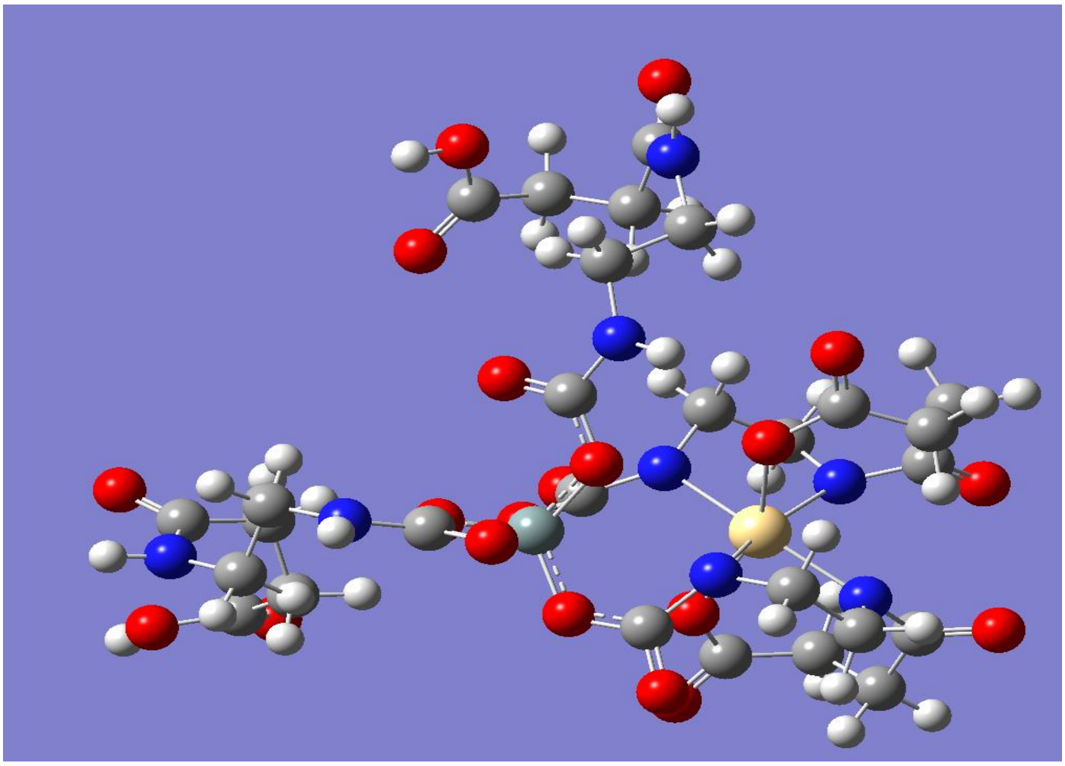

Figure 31. Molecular projection of rha-pa-cd-O1(1)

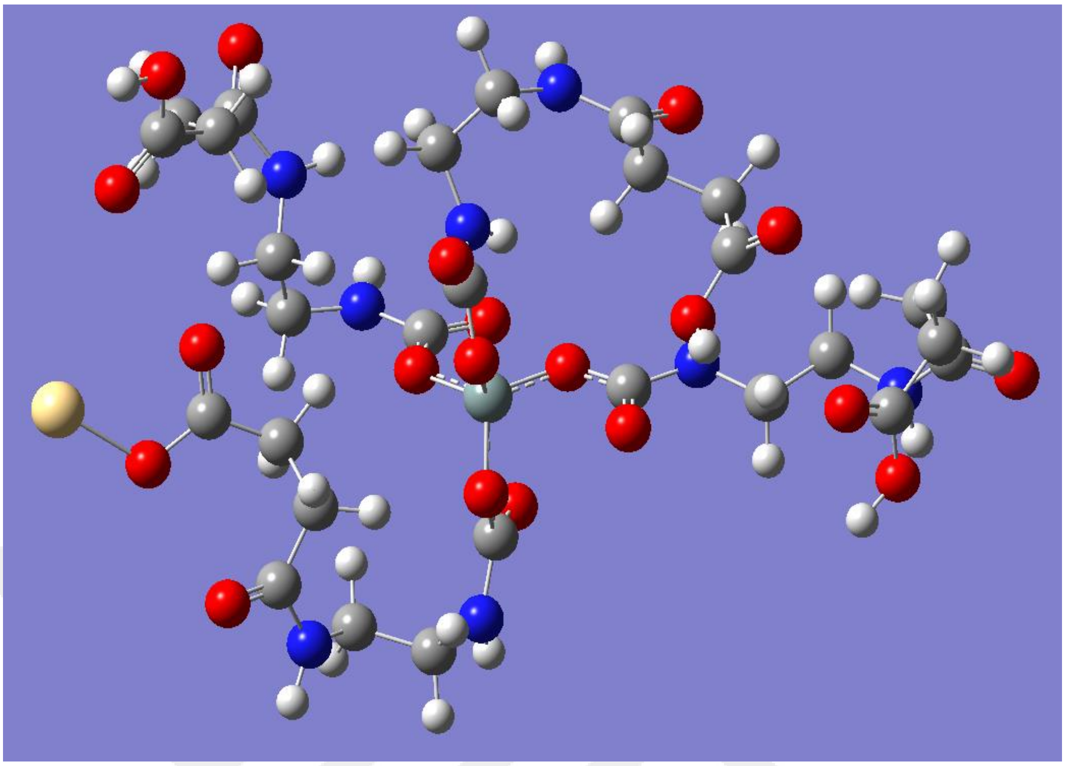

Figure 32. Molecular projection of rha-pa-cd-O1(2)

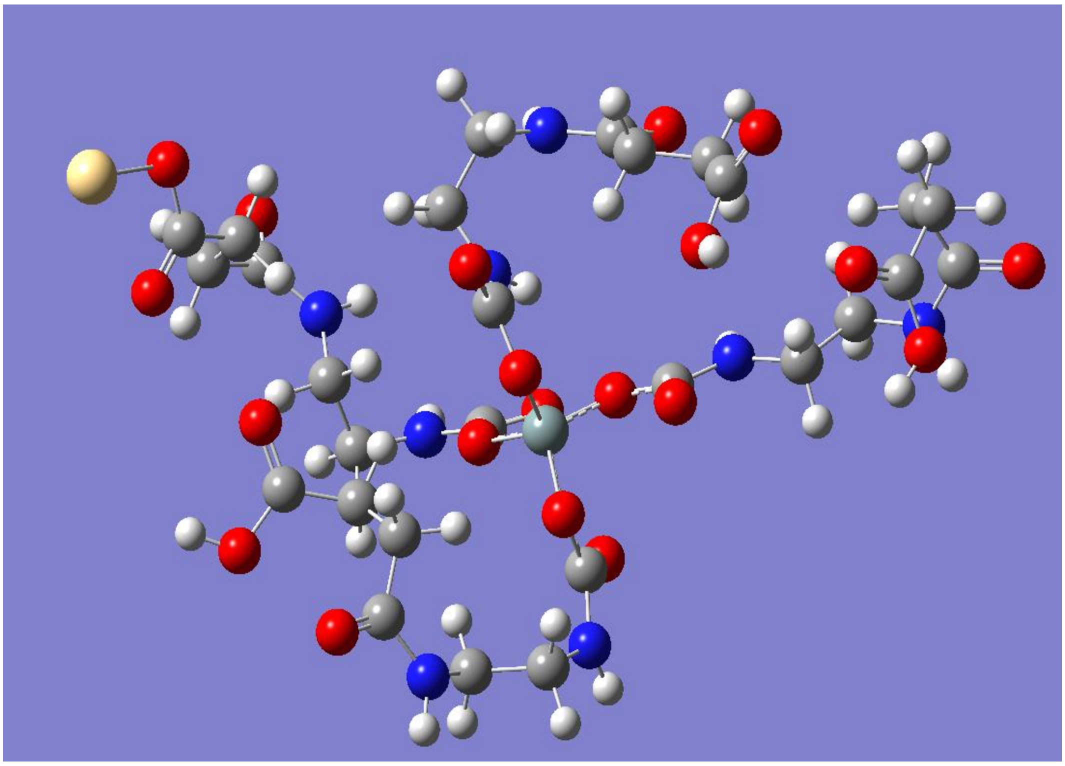

Figure 33. Molecular projection of rha-pa-cd-O1(3)

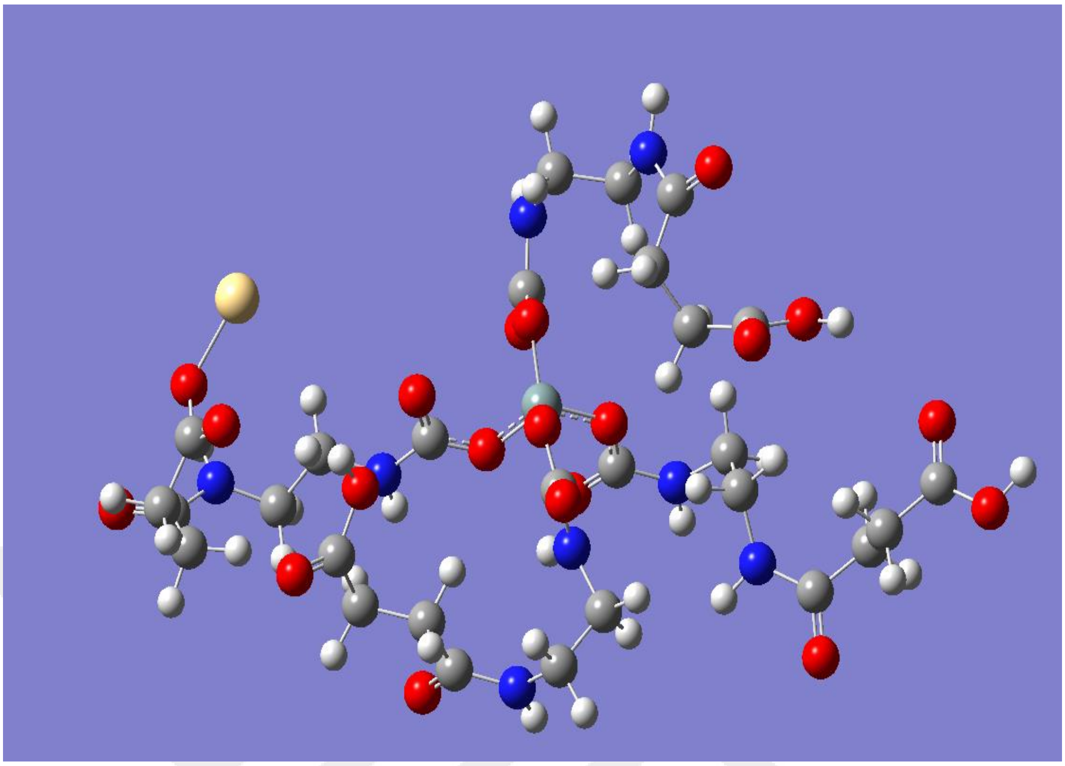

Figure 34. Molecular projection of rha-pa-cd-O1(4)

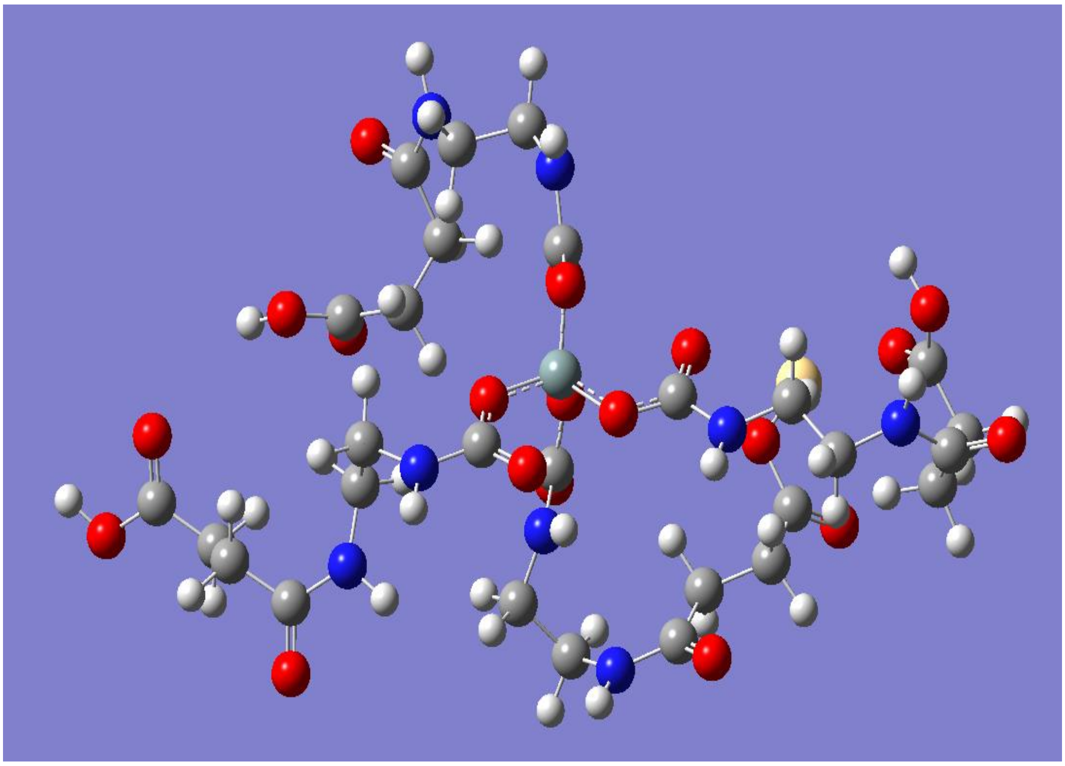

Figure 35. Molecular projection of rha-pa-cd-O2(1)

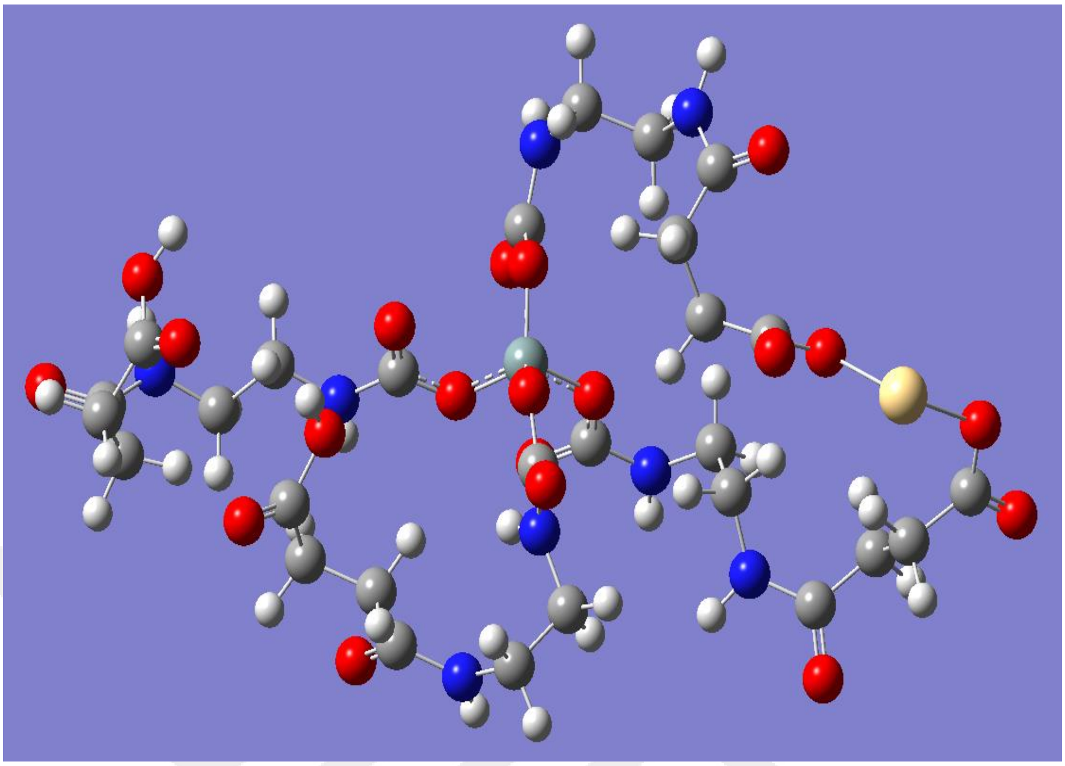

Figure 36. Molecular projection of rha-pa-cd-O2(2)

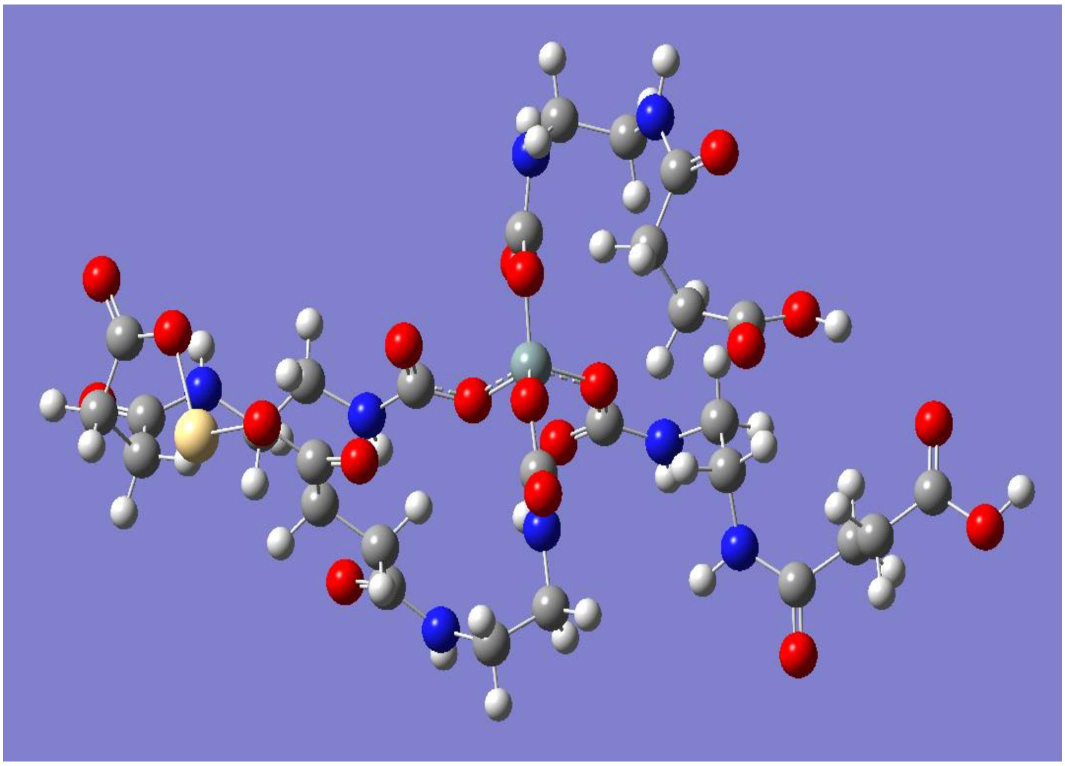

Figure 37. Molecular projection of rha-pa-cd-O2(3)

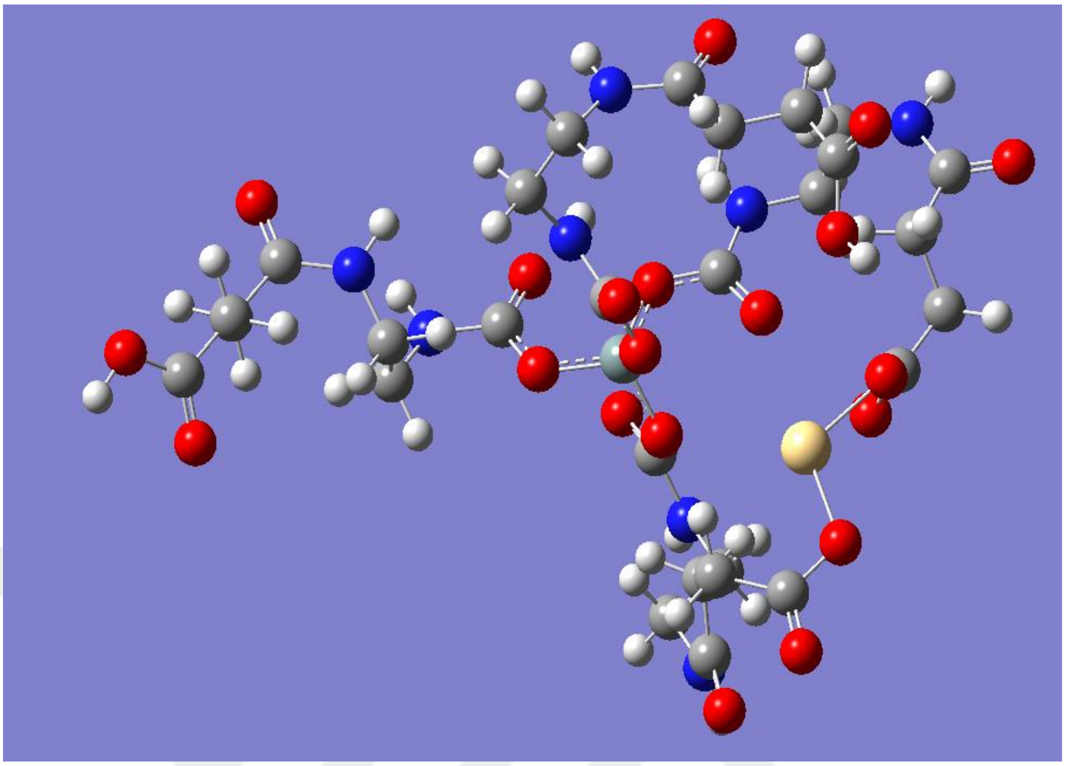

Figure 38. Molecular projection of rha-pa-cd-O2(4)