

CHEMISTRY AND ENVIRONMENT

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MANJERI

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HARMFUL EFFECTS OF OXALIC ACID IN BIOLOGICAL SYSTEMS

Dr. Muhammed Basheer Ummathur

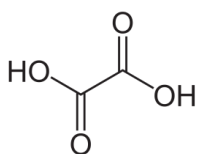
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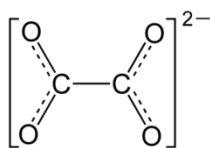
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INTRODUCTION

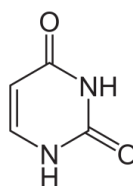
Oxalic acid is the simplest dicarboxylic acid and occurs as the dihydrate $C_2H_2O_4 \cdot 2H_2O$. It is a colourless crystalline solid soluble in water. It is a reducing agent and its deprotonated species, oxalate ion ($C_2O_4^{2-}$), is a chelating agent for metal cations¹. Its main applications include cleaning or bleaching, especially for the removal of rust due to the formation of a stable, water-soluble ferrioxalate ion. Hydrated lanthanide oxalates are formed readily in very strongly acidic solutions in a densely crystalline, easily filtered form, largely free of contamination by non-lanthanide elements. Thermal decomposition of these oxalates gives the oxides, which is the most commonly marketed form of these elements. Oxalic acid is required in our body for the formation of uracil and orotic acid².



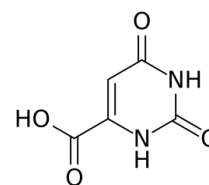
Oxalic acid



Oxalate dianion



Uracil



Orotic acid

ROLE OF OXALIC ACID IN BIOLOGICAL SYSTEM

More than 90% of the oxalic acid consumed is normally excreted through urine. Organic form of oxalic acid, in low concentration, is essential to maintain peristaltic motion in our body. However, when it is processed or cooked, it becomes inorganic form, and may have certain negative effects on the body. Oxalic acid in concentrated form can have harmful effects through contact and ingestion. It is not identified as mutagenic or carcinogenic; there is a possible risk of congenital malformation in the fetus; may be harmful if inhaled, and is extremely destructive to tissue of mucous membranes and upper respiratory tract; harmful if

swallowed; and causes burns if absorbed through the skin or is in contact with the eyes. Symptoms and effects include a burning sensation, cough, wheezing, laryngitis, shortness of breath, spasm, inflammation and edema of the larynx, inflammation and edema of the bronchi, pneumonia and pulmonary edema. In humans, ingested oxalic acid has an oral LD_{Lo} (lowest published lethal dose) of 600 mg/kg. It has been reported that the lethal oral dose is 15 to 30 grams³.

When oxalic acid combines with calcium and other minerals it creates oxalate crystals, which can contribute to kidney stones, gout *etc*⁴. Oxalic acid can also interfere with the absorption of minerals in our diet such as calcium, potassium, and magnesium. Hence, it is advisable for people with certain health conditions to limit its intake through the diet. Oxalic acid can also cause joint pain due to the formation of similar precipitates in the joints⁵.

Normally, calcium and small amounts of oxalate are present in the urinary tract at the same time, but they remain dissolved and cause no problems. However, sometimes they bind to form crystals. In some people, these crystals can lead to the formation of stones, especially when oxalate is high and urine volume is low. Small stones often don't cause any problems, but large stones can cause severe pain, nausea and blood in the urine as they move through the urinary tract. Although there are other types of kidney stones, about 80% are made up of calcium oxalate. For this reason, people who have had one episode of kidney stones may be advised to minimize their consumption of foods high in oxalate. However, oxalate restriction is no longer recommended to every person with kidney stones. This is because most of the oxalate found in urine is produced by the body, rather than absorbed from food. Most urologists now only prescribe a strict low-oxalate diet (less than 50 milligrams per day) for patients who have high levels of oxalate in their urine⁶.

Some claim that a high oxalate intake may be linked to the development of autism⁷. Others say oxalates may be linked to vulvodynia, which is characterized by chronic, unexplained vaginal pain. Elevated levels of oxalate have been found in the urine of patients who have had gastric bypass surgery or other surgeries that alter gut function. This suggests that people who have taken antibiotics or suffer from gut dysfunction may benefit more from a low-oxalate diet.

While many people think about oxalates as some rare and undesirable component of food, oxalates are naturally occurring substances found in a wide variety of foods and they play a supportive role in the metabolism of many plants and animals and in our human

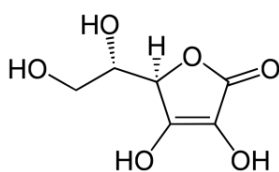
metabolism as well. So in term of our overall health and diet, oxalates are neither rare nor undesirable.

The effects of oxalic acid in the human body, when ingested in foods, flow from its ability to combine chemically with certain metals commonly found in and importance to the human body, such as magnesium and calcium. When oxalic acid combines with such metals, the result is oxalates. Since oxalic acid is not so far as is known today a useful nutrient, it is like all such unneeded components of diet processed by the body to convenient form, those oxalates, and that byproducts is then eventually excreted in the urine.

Some proponents of low-oxalate diets say people are better not consuming foods rich in oxalates, since they may have negative health effects. However, it's not that simple. Many of these are healthy foods that contain important antioxidants, fiber and other nutrients. Therefore, it's not a good idea for most people to completely stop eating high oxalate foods.

Oxalic acid is toxic because of its acidic and chelating properties. It may cause burns, nausea, severe gastroenteritis and vomiting, shock and convulsions. It is especially toxic when ingested, as little as 5 to 15 grams (71 mg/kg) may be fatal to humans.

Oxalic acid can kill by lowering the calcium level in our blood below a critical level. The antidote is calcium gluconate solution. Although foods high in oxalic acid can be avoided, we cannot exclude it entirely from our body because there are other sources. For example, surplus Vitamin C, which the body cannot store, is turned into oxalic acid, and a side effect of effect of taking massive doses of this vitamin may be kidney stones⁸.



Vitamin C

While oxalic acid is a product of the breakdown of vitamin C and may, theoretically, accumulate to form kidney stones, doses of as much as 10 g of vitamin C have not been associated with the increased oxalate stone formation. Some experts caution that anyone who is at increased risk for forming calcium oxalate stone should avoid high doses of vitamin C.

Oxalic acid is a poison that can cause a range of potentially life threatening symptoms. It cause abdominal pain, convulsions, kidney problems, low blood pressure, mouth and throat pain, shock, tremors, vomiting and weak pulse as possible sign of oxalic acid poisoning. First

aid treatment includes drinking water or milk, unless the person is experiencing symptoms that make it difficult to swallow, such as vomiting, convulsions, or decreased alertness. Seek emergency care if these symptoms appear suddenly.

FOODS CONTAINING OXALIC ACID

Oxalic acid occurs naturally in high levels in many common foods, including several vegetables like potatoes, beets, broccoli, carrot and food likes fruits, nuts and legumes and grains, chocolates, beer *etc*⁹. In some of these food items, it tastes pleasantly sour, and in other it's essentially tasteless. Because it binds with some nutrients making them unavailable, for this reason the oxalic acid is often described as an anti-nutrient.

1. *Fruits*:- Blackberries, blueberries, raspberries, strawberries, currants, kiwifruit, concord (purple) grapes, figs, tangerines and plums.
2. *Vegetables*:- Spinach, Swiss chard, beets (root part), beet greens (leaf part), collards, okra, parsley, and leeks are among the most oxalate-dense vegetables. Celery, beans, rutabagas and summer squash are considered moderately dense in oxalates.
3. *Nuts and seeds*:- Almond, cashew and peanuts.
4. *Legumes*:- Soybeans, tofu and other soy products.
5. *Grains*:- Wheat bran, wheat germ, quinoa (a vegetable often used like a grain).
6. *Others*:- Coca, chocolate and black tea.

HOW TO DO A LOW OXALATE DIET

Eat fewer high-oxalate foods

The more oxalate that is absorbed from our digestive tract, the more the oxalate in our urine. High-oxalate foods to limit are spinach, bran flakes, rhubarb, beets, potato chips, French fries, nuts and nut butters.

We do not need to cut other healthy foods that provide some oxalate. In fact, oxalate is practically unavoidable, because most plant food items have some. Often a combination of calcium from foods or beverages with meals and fewer high oxalate foods is required.

Increase the amount of calcium in our diet

Low amounts of calcium in our diet will increase the chances of forming calcium oxalate kidney stones. Many people are afraid to eat calcium because of the name “calcium

oxalate stones". However, calcium binds oxalate in the intestines. A diet rich in calcium helps reduce the amount of oxalate being absorbed by our body, so stones are less likely to form. Eat calcium rich foods and beverages every day (2 to 3 servings) from dairy foods or other calcium rich foods.

Also, eating high calcium foods at the same time as high oxalate food is helpful; for example have low fat cheese with a spinach salad or yogurt with berries. If we take a calcium supplement, calcium citrate is the preferred form.

Limit the vitamin C content of our diet

Oxalate is produced as an end product of vitamin C (Ascorbic acid) metabolism. Large doses of Vitamin C may increase the risk of kidney stone formation. If we are taking a supplement, do not take more than 500 mg of Vitamin C daily.

Drink the right amount of fluids every day

It's very important to drink plenty of liquids. Our goal should be 10-12 glasses a day. At least 5-6 glasses should be water. We may also want to consider drinking lemonade. Research suggests that lemonade may be helpful in reducing the risk of calcium oxalate stone formation¹⁰.

REFERENCES

1. L. G. Wade; *Organic Chemistry*, 8th Edition, Pearson, Boston, 2017.
2. D. S. Robertson; The Function of Oxalic Acid in Human Metabolism, *Clin. Chem. Lab. Med.*, 2011, 49(9), 1405-1412.
3. V. Veer and R. Gopalakrishnan; *Herbal Insecticides, Repellents and Biomedicines: Effectiveness and Commercialization*, Springer, 2016.
4. H. Han, A. M. Segal, J. L. Seifter and J. T. Dwyer; Nutritional Management of Kidney Stones (Nephrolithiasis), *Clin. Nutr. Res.*, 2015, 4(3), 137–152.
5. E. C. Lorenz, C. J. Michet, D. S. Milliner and J. C. Lieske; Update on Oxalate Crystal Disease, *Curr. Rheumatol Rep.*, 2013, 15(7), 340-348.

6. M. D. Sorensen; Calcium Intake and Urinary Stone Disease, *Transl. Androl. Urol.*, 2014, 3(3), 235–240.
7. K. J. Porowski, T. Zoch-Zwierz, W. Wasilewska, J. Kadziela-Olech, H. Kulak, W. Owens, S. Piotrowska and J. K. Maciej; A Potential Pathogenic Role of Oxalate In Autism, *Europ. J. Paed. Neur.*, 2011, 16, 485-491.
8. P. M. Ferraro, E. N. Taylor, G. Gambaro and G. C. Curhan; Vitamin D Intake and the Risk of Incident Kidney Stones, *J. Urol.*, 2017, 197(2), 405–410.
9. O.S. Fatoki, H. F. Linskens and J. F. Jackson; *Vegetables and Vegetable Products: Modern Methods of Plant Analysis*, Springer, Berlin, Heidelberg, 1994.
10. Z. Gul and M. Monga; Medical and Dietary Therapy for Kidney Stone Prevention, *Korean J. Urol.*, 2014, 55(12), 775–779.

FUEL FROM PLASTIC WASTE

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The present rate of economic growth is unsustainable without saving of fossil energy like crude oil, natural gas, or coal. There are many alternatives to fossil energy such as biomass, hydropower, and wind energy. Also, suitable waste management strategy is another important aspect. Development and modernization have brought about a huge increase in the production of all kinds of commodities, which indirectly generate waste. Plastics have been one of the materials because of their wide range of applications due to versatility and relatively low cost. Recycling can be divided into four categories: primary, secondary, tertiary, and quaternary. As calorific value of the plastics is comparable to that of fuel, so production of fuel would be a better alternative. So the methods of converting plastic into fuel, specially pyrolysis and catalytic degradation, are discussed in detail and a brief idea about the gasification is also included. Thus conversion of plastic waste into fuel can address the problem of plastic waste disposal and shortage of conventional fuel and thereby help in promotion of sustainable environment.

1. Introduction

The increase in use of plastic products caused by sudden growth in living standards had a remarkable impact on the environment. Plastics have now become indispensable materials, and the demand is continually increasing due to their diverse and attractive applications in household and industries. Mostly, thermoplastics polymers make up a high proportion of waste, and this amount is continuously increasing around the globe. Hence, waste plastics pose a very serious environmental challenge because of their huge quantity and disposal problem as thermoplastics do not biodegrade for a very long time.

The consumption of plastic materials is vast and has been growing steadily in view of the advantages derived from their versatility, relatively low cost, and durability (due to their high

chemical stability and low degradability). Some of the most used plastics are polyolefins such as polyethylene and polypropylene, which have a massive production and consumption in many applications such as packaging, building, electricity and electronics, agriculture, and health care [1]. In turn, the property of high durability makes the disposal of waste plastics a very serious environmental problem, land filling being the most used disposal route. Plastic wastes can be classified as industrial and municipal plastic wastes according to their origins; these groups have different qualities and properties and are subjected to different management strategies [2, 3].

Plastic materials production has reached global maximum capacities leveling at 260 million tons in 2007, where in 1990 the global production capacity was estimated at 80 million tons [1]. Plastic production is estimated to grow worldwide at a rate of about 5% per year [4]. Polymer waste can be used as a potentially cheap source of chemicals and energy. Due to release of harmful gases like dioxins, hydrogen chloride, airborne particles, and carbon dioxide, incineration of polymer possesses serious air pollution problems. Due to high cost and poor biodegradability, it is also undesirable to dispose by landfill.

Recycling is the best possible solution to the environmental challenges facing the plastic industry. These are categorized into primary, secondary, tertiary, and quaternary recycling. Chemical recycling, that is, conversion of waste plastics into feedstock or fuel has been recognized as an ideal approach and could significantly reduce the net cost of disposal. The production of liquid hydrocarbons from plastic degradation would be beneficial in that liquids are easily stored, handled, and transported. However, these aims are not easy to achieve [4]. An alternative strategy to chemical recycling, which has attracted much interest recently, with the aim of converting waste plastics into basic petrochemicals is to be used as hydrocarbon feedstock or fuel oil for a variety of downstream processes [3]. There are different methods of obtaining fuel from waste plastic such as thermal degradation, catalytic cracking, and gasification [3, 5].

2. Methods of Converting Plastic to Fuel

2.1. Pyrolysis/Thermal Degradation

Pyrolysis is a process of thermal degradation of a material in the absence of oxygen. Plastic is fed into a cylindrical chamber. The pyrolytic gases are condensed in a specially designed

condenser system, to yield a hydrocarbon distillate comprising straight and branched chain aliphatic, cyclic aliphatic, and aromatic hydrocarbons, and liquid is separated using fractional distillation to produce the liquid fuel products. The plastic is pyrolysed at 370°C–420°C.

The essential steps in the pyrolysis of plastics involve (1) evenly heating the plastic to a narrow temperature range without excessive temperature variations, (2) purging oxygen from pyrolysis chamber, (3) managing the carbonaceous char by-product before it acts as a thermal insulator and lowers the heat transfer to the plastic, (4) careful condensation and fractionation of the pyrolysis vapors to produce distillate of good quality and consistency.

Advantages of pyrolysis process [5] are (a) volume of the waste is significantly reduced (<50–90%), (b) solid, liquid, and gaseous fuel can be produced from the waste, (c) storable/transportable fuel or chemical feed stock is obtained, (d) environmental problem is reduced, (e) desirable process as energy is obtained from renewable sources like municipal solid waste or sewage sludge, (f) the capital cost is low. There are different types of pyrolysis process. Conventional pyrolysis (slow pyrolysis) proceeds under a low heating rate with solid, liquid, and gaseous products in significant portions [5]. It is an ancient process used mainly for charcoal production. Vapors can be continuously removed as they are formed [5]. The fast pyrolysis is associated with tar, at low temperature (850–1250 K) and/or gas at high temperature (1050–1300 K). At present, the preferred technology is fast or flash pyrolysis at high temperatures with very short residence time [5]. Fast pyrolysis (more accurately defined as thermolysis) is a process in which a material, such as biomass, is rapidly heated to high temperatures in the absence of oxygen [5].

Potential Applications of Pyrolysis Products

The liquid oil produced from the catalytic pyrolysis of different types of plastic feedstock has a high number of aromatic, olefin, and naphthalene compounds that are found in petroleum products. Moreover, the HHV of the produced liquid oil has been found in the range of 41.7–44.2 MJ/kg which is very close to the energy value of conventional diesel. Thus, the pyrolysis liquid oil produced from various plastic wastes has the potential to be used as an alternative source of energy. The production of electricity is achievable using pyrolysis liquid oil in a diesel engine used. Pyrolytic liquid oil can also be used as an alternative in a kerosene stove. Moreover, the produced aromatic compounds can be used as raw material for polymerization in various chemical industries. Furthermore, various researchers utilized the produced liquid oil as

transportation fuel after blending with conventional diesel at different ratios. The studies were carried out to explore the potential of produced liquid oil in the context of engine performance and vehicle exhaust emission and it has been reported that 20:80% blend ratio of pyrolytic liquid oil and conventional diesel, respectively, gave similar engine performance results than conventional diesel. Moreover, at the same blended ratio the exhaust emissions were also similar, however the exhaust emissions increased with the increase in the blended amount of pyrolysis oil.

2.2. Catalytic Degradation

In this method, a suitable catalyst is used to carry out the cracking reaction. The presence of catalyst lowers the reaction temperature and time. The process results in much narrower product distribution of carbon atom number and peak at lighter hydrocarbons which occurs at lower temperatures. The cost should be further reduced to make the process more attractive from an economic perspective. Reuse of catalysts and the use of effective catalysts in lesser quantities can optimize this option. This process can be developed into a cost-effective commercial polymer recycling process for solving the acute environmental problem of disposal of plastic waste. It also offers the higher cracking ability of plastics, and the lower concentration of solid residue in the product [3].

Various chemical processes involved in the Catalytic Degradation are given below.

1. Initiation. Initiation may occur on some defected sites of the polymer chains. For instance, an olefinic linkage could be converted into an on-chain carbonium ion by proton addition: The polymer chain may be broken up through β -emission: Initiation may also take place through random hydride-ion abstraction by low-molecular-weight carbonium ions. The newly formed on-chain carbonium ion then undergoes β -scission.

2. Depropagation. The molecular weight of the main polymer chains may be reduced through successive attacks by acidic sites or other carbonium ions and chain cleavage, yielding an oligomer fraction (approximately C_{30} – C_{80}). Further, cleavage of the oligomer fraction probably by direct β -emission of chain-end carbonium ions leads to gas formation on one hand and a liquid fraction (approximately C_{10} – C_{25}) on the other.

3. *Isomerization.* The carbonium ion intermediates can undergo rearrangement by hydrogen- or carbon-atom shifts, leading to a double-bond isomerization of an olefin: Other important isomerization reactions are methyl-group shift and isomerization of saturated hydrocarbons.

4. *Aromatization.* Some carbonium ion intermediates can undergo cyclization reactions. An example is when hydride ion abstraction first takes place on an olefin at a position several carbons removed from the double bond, the result being the formation of an olefinic carbonium ion: The carbonium ion could undergo intramolecular attack on the double bond.

2.3. Gasification

In this process, partial combustion of biomass is carried out to produce gas and char at the first stage and subsequent reduction of the product gases, chiefly CO₂ and H₂O, by the charcoal into CO and H₂. Depending on the design and operating conditions of the reactor, the process also generates some methane and other higher hydrocarbons (HCs). Broadly, gasification can be defined as the thermochemical conversion of a solid or liquid carbon-based material (feedstock) into a combustible gaseous product (combustible gas) by the supply of a gasification agent (another gaseous compound). The gasification agent allows the feedstock to be quickly converted into gas by means of different heterogeneous reaction. If the process does not occur with help of an oxidising agent, it is called indirect gasification and needs an external energy source gasification agent, because it is easily produced and increases the hydrogen content of the combustible gas [5].

A gasification system is made up of three fundamental elements: the gasifier, helpful in producing the combustible gas; the gas clean up system, required to remove harmful compounds from the combustible gas; the energy recovery system. The system is completed with suitable subsystems, helpful to control environmental impacts (air pollution, solid wastes production, and wastewater).

Gasification process represents a future alternative to the waste incinerator for the thermal treatment of homogeneous carbonbased waste and for pretreated heterogeneous waste.

3. Summary

Plastics are “one of the greatest innovations of the millennium” and have certainly proved their reputation to be true. Plastic is lightweight, does not rust or rot, is of low cost, reusable, and conserves natural resources and for these reasons, plastic has gained this much popularity. The literature reveals that research efforts on the pyrolysis of plastics in different conditions using different catalysts and the process have been initiated. However, there are many subsequent problems to be solved in the near future. The present issues are the necessary scale up, minimization of waste handling costs and production cost, and optimization of gasoline range products for a wide range of plastic mixtures or waste.

Huge amount of plastic wastes produced may be treated with suitably designed method to produce fossil fuel substitutes. The method is superior in all respects (ecological and economical) if proper infrastructure and financial support is provided. So, a suitable process which can convert waste plastic to hydrocarbon fuel is designed and if implemented then that would be a cheaper partial substitute of the petroleum without emitting any pollutants. It would also take care of hazardous plastic waste and reduce the import of crude oil.

Challenge is to develop the standards for process and products of postconsumer recycled plastics and to adopt the more advanced pyrolysis technologies for waste plastics, referring to the observations of research and development in this field. The pyrolysis reactor must be designed to suit the mixed waste plastics and small-scaled and middle-scaled production. Also, analysis would help reducing the capital investment and also the operating cost and thus would enhance the economic viability of the process

References

1. T. S. Kpere-Daibo, *Plastic catalytic degradation study of the role of external catalytic surface, catalytic reusability and temperature effects [Doctoral thesis]*, University of London Department of Chemical Engineering University College London, WC1E 7JE.
2. A. G. Buekens and H. Huang, “Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes,” *Resources Conservation and Recycling*, vol. 23, no. 3, pp. 163–181, 1998. View at: [Publisher Site](#) | [Google Scholar](#)

3. A. K. Panda, R. K. Singh, and D. K. Mishra, “Thermolysis of waste plastics to liquid fuel. A suitable method for plastic waste management and manufacture of value added products—a world prospective,” *Renewable and Sustainable Energy Reviews*, vol. 14, no. 1, pp. 233–248, 2010. View at: [Publisher Site](#) | [Google Scholar](#)
4. S. M. Al-Salem, P. Lettieri, and J. Baeyens, “The valorization of plastic solid waste (PSW) by primary to quaternary routes: from re-use to energy and chemicals,” *Progress in Energy and Combustion Science*, vol. 36, no. 1, pp. 103–129, 2010. View at: [Publisher Site](#) | [Google Scholar](#)
5. R. P. Singhad, V. V. Tyagib, T. Allen et al., “An overview for exploring the possibilities of energy generation from municipal solid waste (MSW) in Indian scenario,” *Renewable and Sustainable Energy Reviews*, vol. 15, no. 9, pp. 4797–4808, 2011. View at: [Publisher Site](#) | [Google Scholar](#)

WHAT INSIDE THE SOIL?

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Soil chemistry is the study of soil's chemical properties. Mineral composition, organic matter, and environmental conditions all influence soil chemistry. J. Thomas Way, a consulting chemist for the Royal Agricultural Society in England, conducted numerous tests on how soils exchange ions in the early 1850s and he is considered the father of soil chemistry.

Soil chemistry was primarily concerned with chemical processes in the soil that contribute to pedogenesis or effect plant growth until the late 1960s. Concerns regarding environmental pollution, organic and inorganic soil contamination, and potential ecological and environmental health problems have developed since then. As a result, in soil chemistry, the focus has changed from pedology and agricultural soil science to environmental soil science.

Environmental soil chemistry

Predicting the fate of pollutants and the methods by which they are initially introduced into the soil requires a thorough understanding of environmental soil chemistry. When a chemical is exposed to the soil environment, it can undergo a variety of chemical reactions that might increase or decrease the toxicity of the contaminant. Adsorption/desorption, precipitation, polymerization, dissolution, complexation, and oxidation/reduction are examples of these processes. Scientists and engineers working on environmental restoration frequently overlook these effects. Understanding these processes allows us to more accurately forecast the fate and toxicity of contaminants, as well as build scientifically sound and cost-effective remediation techniques.

Soils transport and move water, house thousands of bacteria and other animals, and contain a variety of worn rock and mineral combinations. The chemical makeup of soil changes as soils and minerals weather over time. Humans, on the other hand, affect the chemistry of soils faster than anything else.

Ion Exchange

The flow of cations (positively charged elements such as calcium, magnesium, and sodium) and anions (negatively charged elements such as chloride and compounds such as nitrate) through soils is known as ion exchange. Cation exchange is far more widespread in the United States.

Cation exchange is the process of a cation in a water solution around a soil particle exchanging with another cation adhered to the clay surface. The number of cations in the soil water solution is significantly less than the number connected to soil particles.

The cation exchange capacity

The cation exchange capacity is the total quantity of positive charges that the soil can absorb (CEC). The rate at which nutrients travel through the profile is influenced by CEC. A soil with a low CEC is substantially less fruitful than one with a high CEC since it can't hold as many nutrients and has fewer clays. It's crucial to apply fertiliser in small amounts if your soil has a low CEC so that it doesn't permeate into the groundwater. A soil with a low CEC is less able to hold spilt chemicals.

Soil pH

The pH of the soil is a measurement of its acidity or alkalinity. pH levels range from 1 to 14, with acidic values ranging from 0 to 7 and alkaline values ranging from 7 to 14. Soils are normally rated from 4 to 10 on a scale of one to ten. Understanding how quickly reactions occur in the soil, as well as the pH, is one of the most critical properties involved in plant growth. The element iron, for example, becomes less accessible to plants when the pH rises. This leads to iron shortage issues. Crops like values of 5.5-8, but the value varies depending on the crop. The pH of soil is determined by the parent material used in its development, although people can alter it to better suit plant growth. Soil pH also affects organisms.

Sorption and Precipitation

Different nutrients and ions can be captured by soil particles. Sorption is the process through which one substance absorbs or retains the properties of another. Soils with high sorption might hold a lot of extra environmental toxins, such as phosphorus, on the particles in this situation. When a nutrient or chemical in the soil solution (water around soil particles) turns into a solid, soil precipitation occurs. If the soils are extremely saline, this is critical. Soil chemists investigate the speed of these reactions under a variety of circumstances.

Soil Organic Matter Interactions

Soil chemists also study soil **organic matter** (OM), which are materials derived from the decay of plants and animals. They contain many hydrogen and carbon compounds. The arrangement and formation of these compounds influence a soils ability to handle spilt chemicals and other pollutants.

Soil structure

Soil structure refers to the way soil is arranged in the solid portions of the soil as well as the pore space between them. The arrangement of soil pores between individual soil granules is governed by how they clump, bind together, and aggregate. Water and air circulation, biological activity, root growth, and seedling emergence are all influenced by soil. Soil structures come in a variety of shapes and sizes. It is a dynamic and complicated system that is influenced by a variety of circumstances.

The arrangement of the solid parts of the soil and the pore spaces between them is referred to as soil structure. Aggregation occurs when soil particles interact through rearrangement, flocculation, and cementation. Precipitation of oxides, hydroxides, carbonates, and silicates; biological activity products (such as biofilms, fungal hyphae, and glycoproteins); multivalent cation ionic bridging between negatively charged particles (both clay minerals and organic compounds); and interactions between organic compounds are all beneficial (hydrogen bonding and hydrophobic bonding).

Most types of cultivation degrade soil structure because the related mechanical mixing compacts and shears aggregates and fills pore spaces, as well as exposing organic materials to

a faster rate of decomposition and oxidation. A further consequence of continued cultivation and traffic is the development of compacted, impermeable layers or 'pans' within the profile.

The disintegration of aggregates and dispersion of clay material as a result of fast soaking is frequently linked to the degradation of soil structure during irrigation. This is especially true if the soils are sodic, meaning the cations bonded to the clays have a high exchangeable sodium percentage (ESP). When particles are wet, high sodium levels (in comparison to high calcium levels) lead them to reject one another, causing aggregates to disaggregate and disperse. If irrigation allows saline water (even at low concentrations) to enter the soil, the ESP will rise.

To protect and improve soil structure, a variety of treatments are used. Increase organic content by incorporating pasture phases into cropping rotations; reduce or eliminate tillage and cultivation in cropping and pasture activities; avoid soil disturbance during periods of excessive dry or wet when soils may tend to shatter or smear; and ensure sufficient ground cover to protect the soil from raindrop impact, according to the NSW Department of Land and Water Conservation. It may be advised in irrigated agriculture to use gypsum (calcium sulphate) to replace sodium cations with calcium and so reduce ESP or sodicity, avoid quick wetting, and avoid disturbing soils when they are too wet or dry.

Grades of soil structure

The degree of aggregation, or grade of structure, is defined as the difference between cohesion* inside aggregates and adhesion* between aggregates. Because these properties change depending on the moisture content of the soil, the grade of building should be decided when the soil is neither too moist nor excessively dry. The following are the four major structure grades, ranging from 0 to 3.

0 Structureless has no observable aggregation or no definite orderly arrangement of natural lines of weakness, such as:

- Massive structure (coherent) where the entire soil horizon appears cemented in one great mass;
- Single-grain structure (non-coherent) where the individual soil particles show no tendency to cling together, such as pure sand;

1. Weak structure is made up of indistinct aggregates that are difficult to see in place. When the soil material is removed from the profile, it is broken down into a mixture of relatively few whole aggregates, many fractured aggregates, and a lot of unaggregated material;
2. In undisturbed soil, moderate structure is well developed from discrete aggregates that are somewhat durable and visible but not distinct. The soil material breaks down into a mixture of numerous distinct whole aggregates, some fragmented aggregates, and minimal unaggregated material when taken from the profile;
3. Strong structure is made up of discrete aggregates that are long-lasting and visible in undisturbed soil. When removed from the profile, the soil material consists very largely of entire aggregates and includes few broken ones and little or no non-aggregated material.

Classes and types of soil structure

By definition, class of structure describes the average size of individual aggregates. Usually, five distinct classes may be recognized in relation to the type of soil structure from which they come. They are:

- Very fine or very thin;
- Fine or thin;
- Medium;
- Coarse or thick;
- Very coarse or very thick.

By definition, type of structure describes the form or shape of individual aggregates. Generally, soil technicians recognize seven types of soil structure, but here only four types are used. They are rated from 1 to 4 as follows:

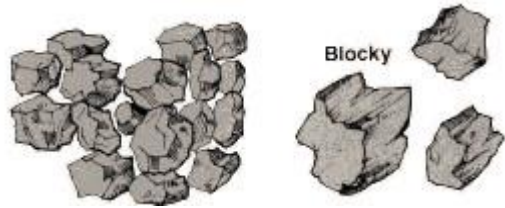
1. Granular and crumb structures are individual particles of sand, silt and clay grouped together in small, nearly spherical grains. Water circulates very easily through such soils. They are commonly found in



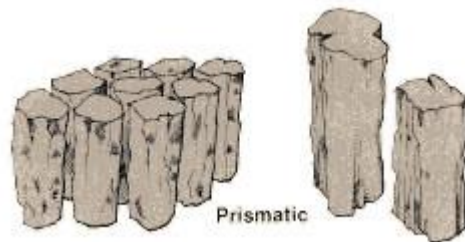
the A-horizon of the soil profile;

2. Blocky and subangular

blocky structures are soil particles that cling together in nearly square or angular blocks having more or less sharp edges. Relatively large blocks indicate that the soil resists penetration and movement of water. They are commonly found in the B-horizon where clay has accumulated;



3. Prismatic and columnar structures are soil particles which have formed into vertical columns or pillars separated by miniature, but definite, vertical cracks. Water circulates with greater difficulty and drainage is poor. They are commonly found in the B-horizon where clay has accumulated;



4. Platy structure is made up of soil particles aggregated in thin plates or sheets piled horizontally on one another. Plates often overlap, greatly impairing water circulation. It is commonly found in forest soils, in part of the A-horizon, and in claypan* soils.



Improving soil structure

Reduced erosion due to increased soil aggregate strength and decreased overland flow; improved root penetration and access to soil moisture and nutrients; improved emergence of

seedlings due to reduced crusting of the surface; and increased water infiltration, retention, and availability due to improved porosity are just a few of the advantages of improving soil structure for plant growth, particularly in an agricultural setting.

In horticulture, productivity from irrigated no-tillage or minimum-tillage soil management declines with time owing to soil structure degradation, which inhibits root growth and water retention. There are a few outliers; it is uncertain why such unique fields preserve structure, but it is linked to high organic matter levels. In these situations, improving soil structure can greatly boost production. Wheat yields in cropping systems can be boosted by 10 kg/ha for every extra millimetre of rain that can enter owing to soil structure, according to the NSW Department of Land and Water Conservation.

Minerals

The mineral components of soil come from the parent rocks, often known as regolith. Minerals account for around 90% of the overall weight of the soil. O, Fe, Si, Al, N, P, K, Ca, Mg, C, H, and other significant elements found in compound form include O, Fe, Si, Al, N, P, K, Ca, Mg, C, H, and others. The creation of primary and secondary minerals can help identify which minerals are present in a rock.

Soil Pores

The interactions of the soil's micropores and macropores are crucial to soil chemistry because they allow water and gaseous components to flow into the soil and into the surrounding atmosphere. Macropores assist in the movement of molecules and substances into and out of micropores. The aggregates themselves are made up of micropores.

Soil Water

Water is necessary for organisms in the soil profile, and in an ideal soil, it partially fills the macropores.

Water moves ions deeper into the lower soil layers, causing the soil to become more Oxidized in other soil horizons, causing leaching of the soil.

Water can also go from a greater water potential to a lower water potential, which can cause capillarity activity and gravitational force due to water adhesion to the soil surface and cohesion among the water molecules.

Air

The three major gases in the atmosphere are oxygen, carbon dioxide, and nitrogen. By volume, oxygen makes up 20% of the atmosphere, nitrogen makes up 79 percent, and CO₂ makes from 0.15 to 0.65 percent. Because of the breakdown of stored organic matter and the quantity of plant roots, CO₂ levels rise as soil depth increases. The presence of oxygen in the soil is beneficial because it aids in the transformation of insoluble stony mass into soluble minerals and organic humification. The air in the soil is made up of the same elements as in the atmosphere, but in different amounts. Chemical processes in bacteria are aided by these gases. Soluble nutrients build up in the soil, making it more productive.

Soil Texture



The ability of the soil to keep its structure, the restriction of water flow, and the contents of the particles in the soil are all influenced by soil texture. Soil texture takes into account all particle kinds, and a soil texture triangle is a diagram that may be used to compute the percentages of each particle type that sum up to 100% for the entire soil profile. These soil divides range not only in size, but also in how they affect some of the most critical aspects determining plant growth, such as soil aeration, workability, water and nutrient transport and availability.

Sand

Sand particles range in size (about 0.05mm-2mm).^[4] Sand is the most coarse of the particle groups. Sand has the largest pores and soil particles of the particle groups. It also drains the most easily. These particles become more involved in chemical reactions when coated with clay.

Silt

Silt particles range in size (about 0.002mm-0.5mm). Silt pores are considered a medium in size compared with the other particle groups. Silt has a texture consistency of flour. Silt particles allow water and air to pass readily, yet retain moisture for crop growth. Silty soil contains sufficient quantities of nutrients both organic and inorganic.

Clay

Clay has particles smallest in size (about<0.002mm) of the particle groups. Clay also has the smallest pores which give it a greater porosity and it does not drain well. Clay has a sticky texture when wet. Some kinds can grow and dissipate or in other words shrink and swell.

Loam

A combination of sand, silt and clay that encompasses soils. It can be named based on the primary particles in the soil composition, ex. sandy loam , clay loam , silt loam, etc.

Soil chemistry is the study of how elements and their compounds are distributed between and within the soil's three main phases: solid, liquid, and gaseous. We want to understand Chemistry of soil and its classification based on its structure. Cation exchange is an important and unifying concept in soil science because it affects the flocculation and dispersion of soils and suspended sediments, the availability and transport of nutrient and contaminant cations, and the management of soil pH.

References

1. Sutton, R. & Sposito, G. Molecular structure in soil humic substances: The new view. *Environ. Sci. Technol.***39**, 9009–9015 (2005).
2. Piccolo, A. & Conte, P. Molecular Size of Humic Substances. Supramolecular Associations Versus Macromolecular Polymers. *Adv. Environ. Res.***3**, 508–521 (1999).

3. Dexter, A. R. Advances in characterization of soil structure. *Soil Tillage Res.***11**, 199–238 (1988).
4. Gupta, V. V. S. R. & Germida, J. J. Soil aggregation: Influence on microbial biomass and implications for biological processes. *Soil Biol. Biochem.***80**, A3–A9 (2015).

POLLUTION AND TREATMENT OF DYE WASTE-WATER

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In recent years with the rapid development of industry, the production of dye waste-water has been increased year by year. Due to complex nature, high concentration, and high colour they are very difficult to biodegrade. As per the United States "Color Index", commodity dyes have been reached tens of thousands. About 60,000 tons of dyes have been directly discharged into the environment in the form of waste each year worldwide and 80% of which are azo dyes. Dyeing Industry, issued in 2001," according to incomplete statistics, the amount of wastewater that have been discharged by textile industry is 900 million tons per year, accounting for the sixth place in industrial discharge ". The dye composition in these printing and dyeing waste-water are complex, high concentration, high colour, difficult to biodegrade substances are many, and contain a variety of organics with biological toxicity and three properties (carcinogenic, teratogenic, mutagenic), so it is often very difficult to achieve the desired effect by using a single treatment technology. The traditional biological treatment has the disadvantage of low processing efficiency and even unable to run, while the physical and chemical treatment has the disadvantages of high processing cost, small processing capacity and harsh operating conditions. So it is very urgent to develop a new treatment process which is effective for this kind of waste-water which can meet more and more stringent discharge standards and achieve the purpose of comprehensive treatment. On applying CWO technology to the treatment of dye waste-water, especially azo dye waste-water, has great environmental significance, theoretical significance and practical application value.

Types of dyes

There are so many dyes with complex structures. There are more than 5,000 varieties of dyes with different chemical structures have been used world-wide. Dyes are classified according to their methods of application and chemical structure. The names of commercial dyes are mostly classified according to their application, while the classification by chemical structure directly represents the characteristics and commonness of dye structure. According to the chemical structure of dyes they are mainly classified to eight

categories: azo dyes, anthraquinone dyes, indigo dyes, phthalocyanine dyes, sulfur dyes, Jia Chuan dyes, triaryl methane dyes, heterocyclic dyes. According to the application based on classification of dyes they are mainly divided into fourteen categories: reactive dyes, acid dyes, direct dyes, insoluble azo dyes, vat dyes (refers to insoluble), soluble vat dyes, sulfur dyes, acid mordant dyes and acid medium dyes, oxidation dyes, polycondensation dyes, disperse dyes, basic dyes and cationic dyes, fluorescent dyes, fluorescent brighteners. Neutral dyes and cationic dyes are two kinds of dyes which are singled out from acid dyes and alkaline dyes, respectively. Among them acid dyes, reactive dyes, cationic dyes, alkaline dyes, direct dyes, vector dyes and neutral dyes are generally water-soluble dyes and acid dyes, reactive dyes, cationic dyes and basic dyes have a higher solubility in water, and the solubility of direct dyes, vector dyes and neutral dyes is slightly poor; generally ice dye, disperse dyes, vat dyes and sulfur dyes are insoluble in water. In the molecular structure of reactive dyes there are reactive groups, which can form covalent bonds with hydroxyl groups on cellulose fibers, protein fibers and amine groups on polyamide fibers under appropriate conditions and combine into a "dye-fiber" as a whole. The reactive dyes have such a large proportion compared with other cellulose fiber dyes because it has the advantages of complete chromatography, bright color, excellent fastness to washing, simple application process, convenient use and applicability, relatively cheap price, and its structure does not contain carcinogenic aromatic amines and so on. At present, reactive dyes have been able to replace some ice dye, sulfur dye and vat dye, but also suitable for the printing and dyeing needs of cellulose fiber products, which makes it more widely used. Although the reactive dyes have many of the above advantages, they also have the following disadvantages:

(1) Low utilization.

The general utilization rate is only 60%~70%, producing a large amount of coloured sewage, its chromaticity is more than a few thousand times, and the concentration of organic matter is high.

(2) High electrolyte consumption during dyeing.

This causes the increase of chlorine ion concentration in the waste-water, which increases the difficulty of dye waste-water treatment.

(3) The amount of nonferrous wastewater containing salts is large and difficult to treat.

(4) The colour fastness of some types of dyes does not meet market requirements.

Source and characteristics of dye wastewater

Sources of dye wastewater

Wastewater has been discharged by the dye industry, including dye production, and the mixing of various wastewater produced by the reprocessing of natural and man-made fiber materials by printing and dyeing plants, wool spinning plants, knitting plants, silk factories, etc. Printing and dyeing processes generally include pre-treatment (desizing, refining, bleaching, mercerization), dyeing, printing, and finishing. The pretreatment stage (including the process of firing, desizing, boiling, bleaching, mercerizing, etc.) should discharge the desizing wastewater, cooking waste-water, bleaching waste-water and mercerizing waste-water, dyeing process discharge dyeing waste-water, printing process discharge printing waste-water and soap liquid waste-water, finishing process discharge finishing waste-water into water bodies. The printing and dyeing waste-water is a mixture of the above kinds of waste-water.

Components of various printing and dyeing waste-water.

The main Contamination Components in waste-water are Direct dyes, Mordant dyes, Acid dyes, Mordant dyes, Metal complex dyes, Disperse dye Dyes, Carriers, Pigments, Coating material, Primulin bases Dyes, Sulphur Alkali, Soda, Metamarine Vat dye Dye, caustic soda, insurance powder, meta powder, red oil Navto dye Dyes, caustic soda, hydrochloric acid, sodium nitrite, sodium acetate, surfactants Disperse dye Dyes, carriers, powder, surfactants Coating material Pigments, ammonia, sodium alginate, resins, mineral oils

Treatment of textile dye polluted waste- water

There are many techniques have been developed to find an economic and efficient way to treat the dyes in waste water including physical chemical biological, combined treatment processes and other technologies. These technologies have been found to be highly efficient for the textile dyeing waste water. Chemical treatment processes are oxidative process consists of Fentons reagent, Ozonation, Photochemicals, Sodium hypochloride, Cucurbituril and electrochemical destruction. Oxidative processes are the most used method of decolourization by chemical means. This is mainly due to its

simplicity of application. In Physical treatments process adsorption techniques have rapidly gaining prominence as a method of treating aqueous effluent due to their efficiency in the removal of pollutants too stable for conventional methods and economically feasible. Physical process consists of activated carbon peat, wood chips, fly ash and coal mixture silica gel, membrane filtration, ion exchange irradiation electrokinetic coagulation and other materials, such as natural clay and agro-waste materials.

Biological treatment process

The biological treatment is also one of the techniques which is environmentally friendly and pollution free by using various potential organisms. The biological process consists of decolourisation by white-rot fungi, other microbial culture, adsorption by living/dead microbial biomass and anaerobic textile dye bioremediation system.

Alternative measures based on all about cited problems regarding the discharge of effluents into the environment, it is obvious there is a need to find alternative treatments that are effective in removing dyes from effluents. By enhancing the existing effluent treatment plants to reverse osmosis (RO) and the resultant water can be used as fresh water for the region. The industries should switch over to cleaner production technologies (CPT) by using combination of soft flow machines, low salt dyes and membranes filtration. This will effectively reduce the water consumption by 50%. The air dyeing technology is a new dyeing process that uses air instead of water to dye garments, allowing companies to create garments with vivid designs and colours without polluting the water and environment. The air dyeing uses 95% less water, emits 84% less greenhouse gases (GHG) and requires 97% less energy.

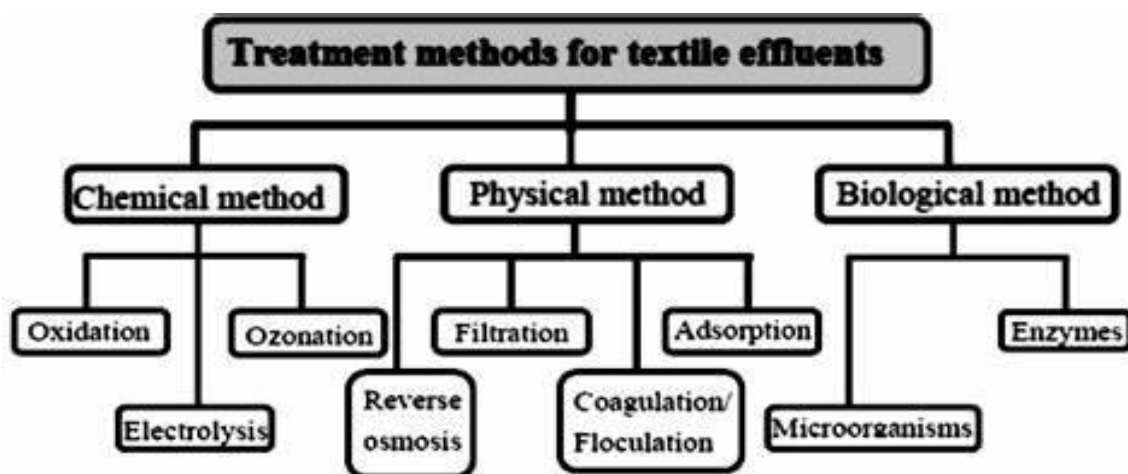


Figure 1 Treatment methods for textile effluents

Conclusion

The production of dye waste-water develops rapidly with the development of modern industry. Dye waste-water is difficult to degrade because of its complex composition, high concentration, high colour and many difficult biodegradable substances. It is important to underline that toxic compound (e.g. toxic aromatic amines, benzidine and its derivatives) can be formed in the environment via transformation of textile dye precursors (e.g., reduction or hydrolysis of textile azo dyes). The textile dye-precursors are introduced in water environment due to industrial production of dyes and industrial production of textile fibres, fabrics and clothes via waste-water. The quality problem of dye content and/or colour in the dye house effluent discharged in water courses can be solved by using of a range of advanced decolorization technologies investigated by the major dye suppliers, textile operators and customers who are under pressure to reduce colour and residual dye levels in their effluents. An alternative to minimize the problems related to the treatment of textile effluents would be the development of more effective dye that can be fixed fiber with higher efficiency decreasing losses on tailings waters and reducing the amount of dye required in the dyeing process, reducing certainly improve the cost and quality of the effluent. The global demand for cheap end products like paints, textile, printing inks, paper, plastics and food will push dye houses to simply react to local regulations by moving operations to another city. Current, the textile dyeing waste water is one of the most important source of pollution. Thetype of this waste-water has the characteristics of higher value of colour, BOD and COD. Complex composition, large emission, widely distributed and difficult degradation. If being directly discharged without being treated, it will bring serious harm to the ecological environment.

References(46)

1. Cheng Y Zhou QX, Ma QY etal.,Advances in dye waste-water technology, *Environmental Pollution Control Technologies and Equipment*, 2003, (46), 56-60.
2. Li Xudong, Yang Yun, Application of Waste Water Treatment Technology and Engineering, *Beijing Machnary Industry Press*, 2003.
3. Zhang yufeng, Teng Jie, Zhang Xueyingetal.,Advances in Technology of Printing and dyeing waste-water Treatment, *Industrial Waste -Water Treatment*, 2003, 23(4),23-27.

ANTI-SNAKE VENOM PROPERTIES OF THERAPEUTIC HERBS

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1. Introduction

Snakebites are a severe public health issue because of their high morbidity rate. Snake venom has been responsible for a large number of deaths around the world [1]. Every year, a large number of people die in India alone. The majority of snake venoms cause severe local tissue damage, which can leave victims disabled for a long time. Anti-venom has been the sole particular treatment available for the past century [2]. But it is insufficient to defend against venom induced haemorrhage, necrosis, and death. Furthermore, the availability and accessibility of anti-venom is limited in many regions. As a result, the hunt for complimentary snakebite treatments continues [3].

Medicinal plants are known to contain pharmacologically active chemicals with therapeutic characteristics. A variety of plants have been studied in the treatment of poisonous bites. Plant extract products are gaining popularity as a result of their easy availability, low cost, and little environmental impact [1]. The present endeavor is to provide an outline regarding the various therapeutic herbs having anti-snake venom properties and the different phytoconstituents responsible for it.

2. Snake venom and clinical complications

Snake venom contains a variety of complex components, including proteins, enzymes, neurotoxins, coagulants, anticoagulants, and other cytotoxic agents. The venom is water soluble, with a specific gravity of 1.03 and an acidic pH [8]. The phosphodiesterase A2 enzyme lyses the cell membrane of erythrocytes, causing them to rupture [4]. Although snake venoms contain a large number of active proteins, in some species, phospholipases A2 (PLA2s) make up the majority of the toxic components and have a wide range of pharmacological effects, including neurotoxicity, cardiotoxicity, myotoxicity, hemolysis,

convulsion, anticoagulation, platelet effect, edema induction, and tissue damage [5]. Victims often have difficulty identifying the snake species that bit them, and clinical signs alone aren't always trustworthy due to overlapping symptoms. The detection of snake venom and venom antibodies in body fluids is critical in snake bite care.

3. Anti-snake venom

Anti-venom serum therapy, which consists of lots of neutralising immunoglobulins, separated from the plasma of animals hyperimmunized against snake venoms is the only specialized treatment available. Its effectiveness stems from its ability to provide patients with antibodies with a high affinity for snake venom, with the goal of eliminating the toxins responsible for envenoming toxicity and slowing the progression of toxic effects caused by snake venom components [6]. However, the anti-venom has certain drawbacks, including a limited ability to treat local effects, the risk of immunological reactions, a high price tag, and limited accessibility in some areas [7, 8]. The neutralisation of systemic effects is usually successful if anti-venom is administered quickly after envenomation; however, neutralisation of local tissue damage is more difficult.

4. Herbal medicines against snake venom

For the treatment of snake bites, a variety of medicinal plants have been suggested. *Acalypha indica*, *Hemidermis indica*, *Pluchea indica*, *Guiera senegalensis*, *Pentaclethra macroloba*, *Tamarindus indica*, *Parkia biglobosa*, and other plants have been found to block a number of different enzymes in snake venom [9-14]. The ancient Indian ayurveda system describes the use of plants in the treatment of snake envenomation. We can find references in the Atharva veda, Rig veda, Charaka, and Sushrutasamithatoo [15]. The plant kingdom in India is rich in medicinal plants, which tribals in India use to treat snake bites. Many studies on various plants have been conducted using knowledge obtained from tribals.

Snake envenomation is most common in India's rural areas, and medicinal plants have long been utilized as a treatment. Natural inhibitors of snake venoms play an important part in the ability to counteract the effects of venom poisons on the body. Animal sera and some plant extracts have long been known to be effective at neutralizing snake venom [16].

Table 1 lists a variety of plant species that are used as traditional medicine to treat snake bites in India. Snake venom can be countered by applying plant extracts to the bite region, chewing leaves or barks, drinking or injecting extracts.

Table 1: List of medicinal plants used against snakebites in India

Plant Species	Family	Part used	Reference
<i>Acalypha indica</i>	Euphorbiaceae)	leaves	17
<i>Alocasia cucullata</i>	Araceae	roots	18
<i>Andrographis paniculata</i>	Acanthaceae	Herb	19 ,20
<i>Annona senegalensis</i>	Annonaceae	Root bark	21
<i>Apuleialeiocarpa</i>	Leguminosae	Root	22
<i>Aristolochia sp.</i>	Aristolochiaceae	roots	23
<i>Picrasmaquassioides</i>	Simaroubaceae	Leaf	24
<i>Emblica officinalis</i>	Euphorbiaceae	roots	25
<i>Piper nigrum</i>	Piperaceae	Flower	26
<i>Persea americana</i>	Lauraceae	seeds	27
<i>Brunfelsiaunifora</i>	Solanaceae	Leaves	28
<i>Casearia sylvestris</i>	Fiacourtiaceae	Seeds	28
<i>Hemidesmus indicus</i>	Asclepiadaceae	Roots	29
<i>Vitex negundo</i>	Verbenaceae	Roots	30
<i>Mimosa pudica</i>	Mimosaceae	herb	31
<i>Mandevillavelutina</i>	Apocynaceae	Roots	32
<i>Vernonia condensata</i>	Compositae	leaves	28
<i>Mucuna pruriens</i>	Papilionacee	seeds	33
<i>Sansevieria zeylanica</i>	Asparagaceae	Whole plant	34
<i>Hibiscus aethiopicus</i>	Malvaceae	Whole plant	35

Some alternatives to antivenom serum are discovered from plant extracts which are rich source of pharmacologically active chemicals. Table 2 lists antiophidian phytochemicals such as plant phenols, alkaloids, triterpenoids, and steroids that have been isolated from a variety of plant species. The interaction of these with toxins/enzymes causes the inhibition or deactivation of venom.

Table 2. Some of the isolated compounds with anti-snake venom activity

Plant species	Compound isolated	Reference
<i>Anisodustanguticus</i>	Anisodamine	36
<i>Aristolochiasp</i>	Aristolochic acid	37
<i>Baccharis trimera</i>	Clerodane diterpenoid	38
<i>Ecliptaprostata</i>	Wedelolactone	39
<i>BrongniartiaPodalyrloides</i>	Edunol	40
<i>Betula alba</i>	Betulin and betulin acid	41
<i>Cordia verbenacea</i>	Rosmarinic acid	42
<i>Cynara scolymus</i>	Cynarin	43
<i>Sapindussaponaria</i>	Flavonoids,	44
<i>Mandevillavelutina</i>	Steroids	45
<i>Mimosa pudica</i>	D-mannitol, sitosterol	46
<i>Hemidesmus indicus</i>	2-hydroxy-4-methoxy benzoic acid	47
<i>Piper umbellatum,</i>	4-nerolidylcatechol	48
<i>Guiera senegalensis</i>	Tannins	10

The study of plant secondary metabolites is an area of great interest as they are abundant and easily available in remote places. Hence the need to investigate the metabolites present in the plants has risen exponentially. Based on the knowledge of ancient culture and traditional practices, many studies have been carried out in this regard and few novel compounds are also been identified. Still many compounds need to be isolated and studied to identify an antivenin that can replace the ASV.

5. References

1. Félix-Silva, J., Silva-Junior, A. A., Zucolotto, S. M., & Fernandes-Pedrosa, M. D. F. (2017). Medicinal plants for the treatment of local tissue damage induced by snake venoms: an overview from traditional use to pharmacological evidence. *Evidence-Based Complementary and Alternative Medicine*, 2017.
2. Xie, C., Slagboom, J., Albulescu, L. O., Bruyneel, B., Still, K., Vonk, F. J., ... & Kool, J. (2020). Antivenom neutralization of coagulopathic snake venom toxins assessed by bioactivity profiling using nanofractionation analytics. *Toxins*, 12(1), 53.
3. Janardhan, B. H. A. V. Y. A., Shrikanth, V. M., Dhananjaya, B. L., & More, S. S. (2014). Antisnake venom properties of medicinal plants. *Int J Pharm Pharm Sci*, 7(S1), 21-6.
4. Enenebeaku, C. K., Umerie, S. C., Nwankwo, M. U., & Enenebeaku, U. E. (2018). Anti-Snake venom Activities of the leaf extracts of *Asystasiagangetica* (L) and *Newbouldialeavis* (p. Beauv). *World News of Natural Sciences*, 16, 33-41.
5. Kini, R. M., Sidhu, S. S., & Laustsen, A. H. (2018). Biosynthetic oligoclonal antivenom (BOA) for snakebite and next-generation treatments for snakebite victims. *Toxins*, 10(12), 534.
6. Gutiérrez, J. M., León, G., & Burnouf, T. (2011). Antivenoms for the treatment of snakebite envenomings: the road ahead. *Biologicals*, 39(3), 129-142.
7. León, G., Herrera, M., Segura, Á., Villalta, M., Vargas, M., & Gutiérrez, J. M. (2013). Pathogenic mechanisms underlying adverse reactions induced by intravenous administration of snake antivenoms. *Toxicon*, 76, 63-76.
8. Shirwaikar, A., Rajendran, K., Bodla, R., & Kumar, C. D. (2004). Neutralization potential of *Viper russellirusselli* (Russell's viper) venom by ethanol leaf extract of *Acalypha indica*. *Journal of Ethnopharmacology*, 94(2-3), 267-273.
9. Gutiérrez, J. M., & Lomonte, B. (1989). Local tissue damage induced by *Bothrops* snake venoms. A review. *Mem. Inst. Butantan*, 51(4), 211-223.
10. Abubakar, M. S., Sule, M. I., Pateh, U. U., Abdurahman, E. M., Haruna, A. K., & Jahun, B. M. (2000). In vitro snake venom detoxifying action of the leaf extract of *Guiera senegalensis*. *Journal of ethnopharmacology*, 69(3), 253-257.

11. Manfred, L. (1977). 7000 Recetasbotánicas a base de plantasmedicinales.
12. Duke, J. A. (2009). *Medicinal Plants of Latin America* (No. 615.321 D8851m Ej. 1 022786). CRC Press.
13. Asuzu, I. U., & Harvey, A. L. (2003). The antisnake venom activities of *Parkia biglobosa* (Mimosaceae) stem bark extract. *Toxicon*, 42(7), 763-768.
14. Camargo, F., Maria Torres, A., Ricciardi, G., Ricciardi, A., & Dellacassa, E. (2011). SDS PAGE: a useful tool for preliminary screening of antisnake activity of plant extracts. *Boletin Latinoamericano y del Caribe de Plantas Medicinales y Aromaticas*, 10(5), 429-434.
15. Whitaker, R., & Whitaker, S. (2012). Venom, antivenom production and the medically important snakes of India. *Current Science*, 635-643.
16. Gupta, Y. K., & Peshin, S. S. (2012). Do herbal medicines have potential for managing snake bite envenomation? *Toxicology international*, 19(2), 89.
17. Kadali, V. N., Kameswara, R. K., & Sandeep, B. V. (2015). Medicinal plants with anti-snake venom property-A review. *The Pharma Innovation*, 4(7, Part A), 11.
18. Wang, W. P. (1986). Preliminary pharmacological studies on the anti-snake-venom action of *Alocasia cucullata*. *Zhong yao tong bao (Beijing, China: 1981)*, 11(2), 53-56.
19. Nazimudeen, S. K., Ramaswamy, S., & Kameswaran, L. (1978). Effect of *Andrographis paniculata* on snake venom induced death and its mechanism. *Indian Journal of Pharmaceutical Sciences*, 40(4), 132-133.
20. Meenatchisundaram, S., Parameswari, G., & Michael, A. (2009). Studies on antivenom activity of *Andrographis paniculata* and *Aristolochia indica* plant extracts against *Daboia russelli* venom by in vivo and in vitro methods. *Indian journal of science and technology*, 2(4), 76-79.
21. Upasani, S. V., Beldar, V. G., Tatiya, A. U., Upasani, M. S., Surana, S. J., & Patil, D. S. (2017). Ethnomedicinal plants used for snakebite in India: a brief overview. *Integrative Medicine Research*, 6(2), 114-130.
22. Pereira, N. A., Ruppelt, B. M., do Nascimento, M. C., Parente, J. P., & Mors, W. B. (1991). An update on plants used against snakebite. In *Brasilianisch-Deutsches Symposium fur Naturstoffchemie, Hanover* (pp. 48-51).

23. Gomes, A., Das, R., Sarkhel, S., Mishra, R., Mukerjee, S., Bhattacharya, S., Gomes, A. (2010). Herbs and herbal constituents active against snake bites. *Indian Journal of Experimental Biology*, 48: 685-708.
24. Makhija, I. K., &Khamar, D. (2010). Anti-snake venom properties of medicinal plants. *Der Pharmacia Lettre*, 2(5), 399-411.
25. Alam, M. I., & Gomes, A. (2003). Snake venom neutralization by Indian medicinal plants (Vitex negundo and Emblica officinalis) root extracts. *Journal of Ethnopharmacology*, 86(1), 75-80.
26. Shenoy, P. A., Nipate, S. S., Sonpetkar, J. M., Salvi, N. C., Waghmare, A. B., & Chaudhari, P. D. (2013). Anti-snake venom activities of ethanolic extract of fruits of Piper longum L.(Piperaceae) against Russell's viper venom: characterization of piperine as active principle. *Journal of Ethnopharmacology*, 147(2), 373-382.
27. Castro, O., Gutiérrez, J. M., Barrios, M., Castro, I., Romero, M., &Umaña, E. (1999). Neutralization of the hemorrhagic effect induced by Bothrops asper (Serpentes: Viperidae) venom with tropical plant extracts. *Revista de biologia tropical*, 47(3), 605-616.
28. Dellacassa, E., Torres, A. M., Ricciardi, G. A., Camargo, F. J., Tressens, S. G., & Ricciardi, A. I. (2014). Anti-venom activity of medicinal plants from south America.
29. Chatterjee, I., Chakravarty, A. K., & Gomes, A. (2006). Daboia russellii and Najakaouthia venom neutralization by lupeol acetate isolated from the root extract of Indian sarsaparilla Hemidesmus indicus R. Br. *Journal of ethnopharmacology*, 106(1), 38-43.
30. Singh, Y., Mishra, P., &Kannoja, P. (2020). Morphology, Phytochemistry and Pharmacological Activity of Vitex negundo: An Overview. *Journal of Drug Delivery and Therapeutics*, 10(3-s), 280-285.
31. Vejayan, J., Ibrahim, H., & Othman, I. (2007). The potential of Mimosa pudica (Mimosaceae) against snake envenomation. *Journal of Tropical Forest Science*, 189-197.
32. Biondo, R., Pereira, A. M. S., Marcussi, S., Pereira, P. S., França, S. C., & Soares, A. M. (2003). Inhibition of enzymatic and pharmacological activities of some snake venoms and toxins by Mandevillavelutina (Apocynaceae) aqueous extract. *Biochimie*, 85(10), 1017-1025.

33. Tan, N. H., Fung, S. Y., Sim, S. M., Marinello, E., Guerranti, R., & Aguiyi, J. C. (2009). The protective effect of *Mucuna pruriens* seeds against snake venom poisoning. *Journal of Ethnopharmacology*, *123*(2), 356-358.
34. Dharmadasa, R. M., Akalanka, G. C., Muthukumarana, P. R. M., & Wijesekara, R. G. S. (2016). Ethnopharmacological survey on medicinal plants used in snakebite treatments in Western and Sabaragamuwa provinces in Sri Lanka. *Journal of Ethnopharmacology*, *179*, 110-127.
35. Hasson, S. S., Al-Balushi, M. S., Said, E. A., Habbal, O., Idris, M. A., Mothana, R. A. A., ... & Al-Jabri, A. A. (2012). Neutralisation of Local Haemorrhage Induced by the Saw-Scaled Viper *Echiscarinatussochureki* Venom Using Ethanolic Extract of *Hibiscus aethiopicus* L. *Evidence-based complementary and alternative medicine*, 2012.
36. Li, Q. B., Pan, R., Wang, G. F., & Tang, S. X. (1999). Anisodamine as an effective drug to treat snakebites. *Journal of Natural Toxins*, *8*(3), 327-330.
37. Vishwanath, B. S., Rao, A. A., & Gowda, T. V. (1987). Interaction of phospholipase A2 from *Viperarusselli* venom with aristolochic acid: a circular dichroism study. *Toxicon*, *25*(9), 939-946.
38. Januário, A. H., Santos, S. L., Marcussi, S., Mazzi, M. V., Pietro, R. C., Sato, D. N., ... & Soares, A. M. (2004). Neo-clerodane diterpenoid, a new metalloprotease snake venom inhibitor from *Baccharis trimera* (Asteraceae): anti-proteolytic and anti-hemorrhagic properties. *Chemico-biological interactions*, *150*(3), 243-251.
39. Melo, P. A., Do Nascimento, M. C., Mors, W. B., & Suarez-Kurtz, G. (1994). Inhibition of the myotoxic and hemorrhagic activities of crotalid venoms by *Ecliptaprostrata* (Asteraceae) extracts and constituents. *Toxicon*, *32*(5), 595-603.
40. Mors, W. B., do Nascimento, M. C., Pereira, B. M. R., & Pereira, N. A. (2000). Plant natural products active against snake bite—the molecular approach. *Phytochemistry*, *55*(6), 627-642.
41. Bernard, P., Scior, T., Didier, B., Hibert, M., & Berthon, J. Y. (2001). Ethnopharmacology and bioinformatic combination for leads discovery: application to phospholipase A2 inhibitors. *Phytochemistry*, *58*(6), 865-874.
42. Ticli, F. K., Hage, L. I., Cambraia, R. S., Pereira, P. S., Magro, Â. J., Fontes, M. R., ... & Sampaio, S. V. (2005). Rosmarinic acid, a new snake venom phospholipase A2

- inhibitor from *Cordia verbenacea* (Boraginaceae): antiserum action potentiation and molecular interaction. *Toxicon*, 46(3), 318-327.
43. Ruppelt, B. M., Pereira, E. F., Gonçalves, L. C., & Pereira, N. A. (1991). Pharmacological screening of plants recommended by folk medicine as anti-snake venom: I. Analgesic and anti-inflammatory activities. *Memórias do Instituto Oswaldo Cruz*, 86, 203-205.
44. da Silva, M. L., Marcussi, S., Fernandes, R. S., Pereira, P. S., Januario, A. H., Franca, S. C., ... & Lourenço, M. V. (2012). Anti-snake venom activities of extracts and fractions from callus cultures of *Sapindussaponaria*. *Pharmaceutical Biology*, 50(3), 366-375.
45. Luzhinskii, V. K., & Semenov, S. R. (1968). Action of meadow geranium against snake venoms. *Nauchnye Trudy, Irkutskii Meditsinskii Institut*, 83, 86-87.
46. Girish, K. S., Mohanakumari, H. P., Nagaraju, S., Vishwanath, B. S., & Kemparaju, K. (2004). Hyaluronidase and protease activities from Indian snake venoms: neutralization by *Mimosa pudica* root extract. *Fitoterapia*, 75(3-4), 378-380.
47. Alam, M. I., Auddy, B., & Gomes, A. (1996). Viper venom neutralization by Indian medicinal plant (*Hemidesmus indicus* and *Pluchea indica*) root extracts. *Phytotherapy Research*, 10(1), 58-61.
48. Núñez, V., Castro, V., Murillo, R., Ponce-Soto, L. A., Merfort, I., & Lomonte, B. (2005). Inhibitory effects of *Piper umbellatum* and *Piper peltatum* extracts towards myotoxic phospholipases A2 from *Bothrops* snake venoms: isolation of 4-nerolidylcatechol as active principle. *Phytochemistry*, 66(9), 1017-1025.

**PLANT FIBRE CELLULOSE POLYMER COMPOSITES AS A GREEN
ALTERNATIVE TO CONVENTIONAL MATERIALS**

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With considerable awareness of preserving the environment, sincere efforts across the globe can be cited in looking for bio-degradable and bio-based sources.

Over the past decade, the concept of utilizing green materials has become more mainstream. Applications of bio-based materials from renewable and bio-degradable sources for preparation of higher valued green chemicals and bio-based products have forced many scientists to investigate the potential use of natural fibers and fiber cellulose as reinforcement materials for green bio-composites. Cellulosic fibers are becoming very interesting for bio-based material development as they possess advantages with their mechanical properties, low density, environmental benefits, renewability, and economic feasibility. Recently, natural-fiber polymer composites have received much attention for different industrial applications because of their low density and renewability. The bio-composites with natural fiber components are derivatives of depleting resources and can be considered to have substantial environmental and economic benefits. The composite materials are finding applications in diverse fields ranging from household, office appliances, power tools, and business equipment to space crafts.

The research and development of new biobased and biodegradable polymers and polymer composites from renewable resources as alternatives to conventional plastics has become an enticing area for both academic and industrial research due to the global concerns over plastic waste and pollution issues. These pro-environmental materials could be a promising solution for the global plastic waste problem. Traditional petroleum-based polymer composites have extensive use in a large number of diverse applications, ranging from small household devices to structural aircraft parts due to their high strength-to-weight ratios as compared to conventional materials. The intensive reliance of plastics has led to an increasing amount of plastic waste in the environment. With the depletion of petroleum resources and growing global environmental concerns over climate change and environmental pollution, the

development of sustainable biobased materials has been growing at a fast pace. Countries including China, France, United Kingdom, Germany, the United States, Japan, and Canada have developed strategies to adapt the circular economy model through sustainable and efficient resource management to help reduce the environmental strain from waste. These countries reinforce these strategies by emphasizing rules and regulations placed on industry manufacturers to develop more sustainable and environmentally friendly products from biobased and biodegradable materials.

This chapter addresses the potential utilization of natural fiber cellulose for the development of green polymer composite materials, with the objective to elucidate the possibility of using these bio composites for various industrial applications.

COMPOSITE

A composite material is composed of at least two materials, which combine to give properties superior to those of the individual constituents. The many component materials and different processes that can be used make composites extremely versatile and efficient. They typically result in lighter, stronger, more durable solutions compared to traditional materials. The primary reason composite materials are chosen for components is because of weight saving for its relative stiffness and strength. For example, carbon-fiber reinforced composite can be five times stronger than 1020 grade steel while having only one fifth of the weight.

The two main components within a composite are the matrix and fiber. The matrix is the base material while the fiber is what reinforces the material. On top of the fiber reinforcements and matrix, composites can also include core materials, fillers, additives and surface finishes to provide unique performance attributes.

Properties of composite materials:

- The tensile strength of composite materials is higher than conventional materials They have better torsion and stiffness properties.
- It has a high fatigue endurance limit (ultimate tensile strength of up to 60%).
- They are 30–45% lighter than aluminum structures designed for the same functional requirements.
- Also has low embedded energy.
- Composites make less noise during operation and provide less vibration.

- Composite materials are additional versatile.

Composite materials are commonly classified at following two distinct levels. Classification of composite materials. (a) Based on matrix materials and (b) based on reinforcement materials. The major composite classes based on matrix materials include organic matrix composites (OMCs), metal matrix composites (MMCs)

and ceramic matrix composites (CMCs). The term organic matrix composite includes two classes of composites, namely polymer matrix composites (PMCs) and carbon matrix composites commonly referred as carbon carbon matrices. Based on reinforcement materials -fiber reinforced composites, laminar composites and particulate composites. Fiber reinforced composites (FRP) can be further divided into those containing discontinuous or continuous fibers. Fiber reinforced composites are composed of fibers embedded in matrix material. Laminar composites are composed of layers of materials held together by matrix. Sandwich structures fall under this category. Particulate composites are composed of particles distributed or embedded in a matrix body. The particles may be flakes or in powder form.

POLYMER COMPOSITES

Polymer matrix composites are materials made up of fibers that are embedded in an organic polymer matrix. Polymer matrix composites are classified based on their level of strength and stiffness into two distinct types: Reinforced plastics - confers additional strength by adding embedded fibrous matter into plastics

Advanced Composites - consists of fiber and matrix combinations that facilitate strength and superior stiffness. They mostly contain high-performance continuous fibers such as high-stiffness glass (S-glass), graphite, aramid, or other organic fibers.

The main advantages of polymer matrix composite materials are their strength and stiffness. Other qualities that come with the reinforcement of polymers are as follows: Improved processing, Density control, Thermal Conductivity, Thermal Expansion Control, Flame retardancy, Cost reduction, Greater toughness

Abrasion resistance, Corrosion resistance, High specific strength to weight ratio

Improved fatigue strength, High creep resistance.

Polymer composites have the following advantages:

- Lightweight (potentially very high strength-to-weight ratio)
- High modulus and glass transition temperatures
- Ability to tailor properties for a wide range of applications
- Good fatigue resistance
- Easy to mould and bond to a variety of substrates or other composites
- Low thermal expansion
- Tailorable electrical properties o Insulating composites with non-conductive fillers

BIO COMPOSITES

A biocomposite is a composite material formed by a matrix and a reinforcement of natural fibers. Environmental concern and cost of synthetic fibers have led the foundation of using natural fiber as reinforcement in polymeric composites. The matrix phase is formed by polymers derived from renewable and non-renewable resources. The matrix is important to protect the fibres from environmental degradation and mechanical damage, to hold the fibers together and to transfer the loads on it. In addition, bio fiber are the principal components of bio composites, which are derived from biological origins, for example fibers from crops (cotton, flax or hemp), recycled wood, waste paper, crop processing by-products or regenerated cellulose fiber (viscose/rayon). The interest in bio composites is rapidly growing in terms of industrial applications (automobiles, railway coach, aerospace, military applications, construction, and packaging) and fundamental research, due to its great benefits.

Advantages of bio composites

- Electrical resistance
- Easy process ability
- Less energy requirement in tooling and assembly
- Higher stiffness and strength
- Cheap
- Renewable source
- Completely recyclable
- Corrosion resistance

NATURAL FIBERS

Natural fibers are fibers that are produced by geological processes, or from the bodies of plants or animals. Natural fibers can have different advantages over synthetic reinforcing fibers. Most notably they are biodegradable and renewable. Additionally, they often have low densities and lower processing costs than synthetic materials. The plants which produce cellulose fibers can be classified into bast fibers (flax, hemp, jute, kenaf, and ramie), leaf fibers (abaca, banana, pineapple, and sisal), seed fibers (coir, cotton, and kapok), as well as all other kinds (roots and wood). Many of the plant fibers such as banana, coir, flax, hemp, jute, pineapple, and sisal find applications as resource for industrial materials.

The main chemical components of natural plant fibers are cellulose, lignin, hemicelluloses, pectin, and wax. The components and their percentages vary depending on the type of natural plant fibers as shown in table below,

Fiber	Cellulose (wt%)	Lignin (wt%)	Hemicellulose (wt%)	Pectin (wt%)	Wax (wt%)	Moisture content (wt%)
Jute	61–71.5	12–13	13.6–20.4	0.4	0.5	12.6
Hemp	70.2–74.4	3.7–5.7	17.9–22.4	0.9	0.8	10
Kenaf	31–39	15–19	21.5	–	–	–
Flax	71	2.2	18.6–20.6	2.3	1.7	10
Ramie	68.6–76.2	0.6–0.7	13.1–16.7	1.9	0.3	8
Sunn	67.8	3.5	16.6	0.3	0.4	10
Sisal	67–78	8–11	10.0–14.2	10	2.0	11
Henquen	77.6	13.1	4–8	–	–	–
Cotton	82.7	–	5.7	–	0.6	–
Kapok	64	13	23	23	–	–
Coir	36–43	41–45	10–20	3–4	–	8
Banana	63–67.6	5	19	–	–	8.7
PALF	70–82	5–12	–	–	–	11.8

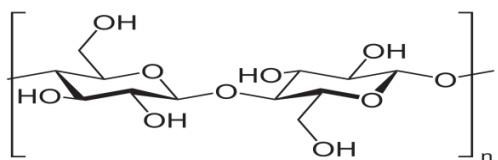
Natural fibers contain low cost, density and weight, less pollution during production resulting in minimal health hazards and eco-friendly nature. Composites reinforced with natural fibers also have a short lifetime when it comes to degradation with limited environmental damage.

CELLULOSE

Cellulose is an organic compound with formula $(C_6H_{10}O_5)_n$. It is polysaccharide made up of several hundreds or thousands of beta glucose unit. Cellulose is present in

primary cell walls of green plants, present in algae, and in oomycetes. Some species of bacteria secrete it to form bio films. On earth, one of the abundant polymers is cellulose. In cotton the cellulose content is about 90%, in wood it is about 40-50% and in dried hemp it is about 57%.

Recently, cellulose has attracted considerable attention as one of the most well-known renewable and sustainable raw materials for obtaining environmentally friendly and biocompatible technological products. Due to its high tensile strength, chemical inertness, biodegradability and renewable nature cellulose is being extensively explored for applications in composite reinforcement, medicine, soft-tissue replacement, artificial bones, dental prostheses, food packaging, building materials etc. It is an odorless and tasteless compound. The appearance is a white powder. It is insoluble in water and most organic solvents. It is chiral and biodegradable. It has a hydrophilic nature and with contact angle of 20-30 degrees. The melting point is found to be 467 degrees in pulse test made by Dauenhauer. Cellulose can be broken down chemically into glucose units by concentrating with mineral acids at high temperature.



Beta glucose units condense through beta-(1, 4) - glycosidic bonds to form cellulose. A contrast with starch is that in starch, alpha-(1, 4)-glycosidic linkage is present. Cellulose is a straight chain polymer. In starch there is coiling and branches but in cellulose, such a coiling is absent. Cellulose molecule adopts an extended and a rather stiff rod like conformation, aided by equatorial conformation of glucose units. The multiple hydrogen bonds on one glucose form hydrogen bonds with oxygen atoms on the same or on a neighbor chain, holding the chains firmly together side by side and forming micro fibrils with high tensile strength. This confers tensile strength in cell walls where cellulose micro fibrils are meshed into a polysaccharide matrix. The high tensile strength of plant stems and that of tree wood also arises from the arrangement of cellulose fibers intimately distributed into the lignin matrix.

Many properties of cellulose depend upon the chain length and degree of polymerization. The chain length of cellulose in wood pulp is between 300 and 1700 units. The bacterial cellulose, cotton and other plant fibers have chain length from 800 to 10,000 units. Cellodextrins have

small length of chain resulting from break down of cellulose. Cellodextrins are soluble in water and organic solvents. Cellulose contains 44.4% carbon, 6.17% hydrogen and 43.39% oxygen. Plant derived cellulose is usually found in a mixture with hemicelluloses, lignin, pectin, and other substances, while bacterial cellulose is quite pure has much higher water content and higher tensile strength due to higher chain lengths.

NATURAL FIBRE REINFORCED BIOCOMPOSITE

Natural plant fiber composites as environmentally attractive materials have been proven and emerged as an alternative to the glass-reinforced composites used in many applications since the 1990s. It is a composite material that consists of three components: the natural fibers as the discontinuous or dispersed phase, the matrix as the continuous phase, and the interface. This is a type of advanced composite group, which makes use of rice husk, rice hull, rice shell, and plastic as ingredients. This technology involves a method of refining, blending, and compounding natural fibers from cellulosic waste streams to form a high-strength fiber composite material in a polymer matrix. It is high-performance fiber composite achieved and made possible by cross-linking cellulosic fiber molecules with resins in the composite material matrix through a proprietary molecular re-engineering process, yielding a product of exceptional structural properties.

Some important areas of applications include:

- Aerospace industry
- Automotive industry
- Construction field
- Consumer goods
- Power industry
- Protective equipment
- Marine infrastructure.

Composite materials are revealing numerous enhancements in distinct material properties since their invention in the last century. Copious amounts of research efforts have been made to discover optimized material to perform in a more effective way for desired applications. Over the past few decades, reinforcements of fibers or particles in the matrix structure of composite materials have revealed outstanding remarks, making them a popular choice for topmost applications. Classifications of composite materials, along with the properties of their

constituent elements, have been studied to understand the potentiality of different composite materials in various fields. Fiber-reinforced composite material was found to be one of the most promising and effective types of composites, as it claims dominance over the majority of applications from topmost fields. Composite materials are fabricated with a number of different techniques, among which every technique is applicable for certain material. Effectiveness of manufacturing technique is dependent on the combination of type and volume of matrix or fiber material used, as each material possesses different physical properties, such as melting point, stiffness, tensile strength, etc. Therefore, manufacturing techniques are defined as per the choice of material. For distinct applications in a variety of fields, certain solitary materials might be replaced with composite materials, depending on the enhancement in its required property. Composite structures have shown improvement in strength and stiffness of material, while the reduction in weight is magnificent. Composites have also revealed some remarkable features such as resistance to impact, wear, corrosion, and chemicals, but these properties are dependent upon the composition of the material, type of fiber, and type of manufacturing technique employed to create it. In accordance with the properties required, composite materials find their applications in many desired fields.

More future research is intended to discover new composite structures with a combination of different variants and adopting new manufacturing techniques.

References

1. Alan J.L, Polymer Composites, *Polym. Compos*, **71**:1529-1622 (2018).
2. Brostow W, Dutta M and Rusek P, J. Modified epoxy coatings on Mild Steel: Tribology and Surface Energy, *Chem. Eur. J*, **46**:2181-2189(2010).
3. Cantwell WJ, Morton J. The impact resistance of composite materials—A review. *Composites*. 1991;**22**(5):347-362. DOI: 10.1016/0010-4361(91)90549-
4. Chanda M, Introduction to Polymer Science and Chemistry, CRC Press, Taylor and Francis Group, FL, USA, *J. Polym. Sci*, 12-14(2006).
5. Elias H.G, An Introduction to Polymer Science, Weinheim: VCH, *J. Polym. Sci. Technol*, 1:19-59(1997).
6. Gowariker V.R, Viswanathan N.V and Sreedher J, *Polymer Science*, New Age International, New Delhi, 12-14(2005).

7. Gupta N, Singh Brar B and Worldebenbet E, Effect of filler addition on the compressive and impact properties of glass fiber reinforced epoxy, *Bull. Mater. Sci*, **24**:219-223(2001).
8. Harsha A.P, An investigation on low stress abrasive wear characteristics of high performance engineering thermoplastic polymers, *Polym. Compos*, **46**:983-991(2011).
9. Ho MP, Wang H, Lee JH, Ho CK, Lau KT, Leng JS, Hui D. Critical factors on manufacturing processes of natural fibre composites. *Composites Part B Engineering*. 2012;**43**:3549-3562. DOI: 10.1016/j.compositesb.2011.10.001
10. Jand B.Z, *Advanced polymer Composites: Principle and Applications*, Material Park: ASM International, *J. Polym. Sci*, **4**:1-12(1994).
11. Jiang L, Zhang J, Wolcott M.P, Mechanical Performance of Polyhydroxyalkanoate (PHA) based Bio-composites, *J. Inorg. Biochem*, **3**:39-52(2015).
12. Joshia SV, Drzal LT, Mohanty AK, Arora S. Are natural fiber composites environmentally superior to glass fiber reinforced composites? *Composites Part A: Applied Science and Manufacturing*. 2004;**35**:371-376. DOI: 0.1016/j.compositesa.2003.09.016
13. Kalpakjian S, Schmid SR. *Manufacturing Engineering and Technology*. International Edition. 4th ed. Prentice Hall, Inc; New Jersey, USA; 2001. ISBN: 0-13-017440-8
14. Malcon P.S, *Polymer chemistry: An introduction*, *Oxford University Press*, **1**, 3-4 (1998).
15. Sanjay MR, Arpitha GR, Naik LL, Gopalakrishna K, Yogesha B. Applications of natural fibers and its composites: An overview. *Natural Resources*. 2016;**7**:108-114. DOI: 10.4236/nr.2016.730
16. Vinod kumar T, Chandrashekar M and Padmanabhan S, Characteristic and Mechanical properties of Reinforced Polymer Composites, Department of Mechanical Engineering, VELS University, *J. Polym. Sci*. **12**:567-601(2006-2007).
17. Yuanjian T, Isaac DH. Impact and fatigue behaviour of hemp fibre composites. *Composites Science and Technology*. 2007;**67**:3300-3307. DOI: 10.1016/j.compscitech.2007.03.039

GREEN CHEMISTRY: DESIGN OF ENVIRONMENTALLY FRIENDLY PROCESSES

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The growing process of Industrialization was accompanied by plenty of changes in the global economy and social structure. However, since the 1940s, environmental issues started to arise associated with the development of industrial activities. Despite environmental issues and concerns, industries have changed their way of conventional production methods and product development traditions by adopting sustainable processes. Over the past few years, chemists have been trained to develop new chemical reactions that are less hazardous to human health and the environment. Green chemistry is an approach to chemistry that looks into maximum productivity and minimum toxicity on human health and the environment.

In 1993, the Toxic Release Inventory of the U.S. Environmental Protection Agency reported that 30 billion pounds of toxic chemicals were released to air, land, and water (Figure 1). While this information covers the release of hazardous compounds from a variety of industrial sectors which include only 1% of chemicals available today. Out of the industrial sectors, chemical manufacturing industries are reasonably the largest releaser of chemicals to the environment, delivering more than 4 times as many pounds to the environment as the next highest sector (Figure 2).

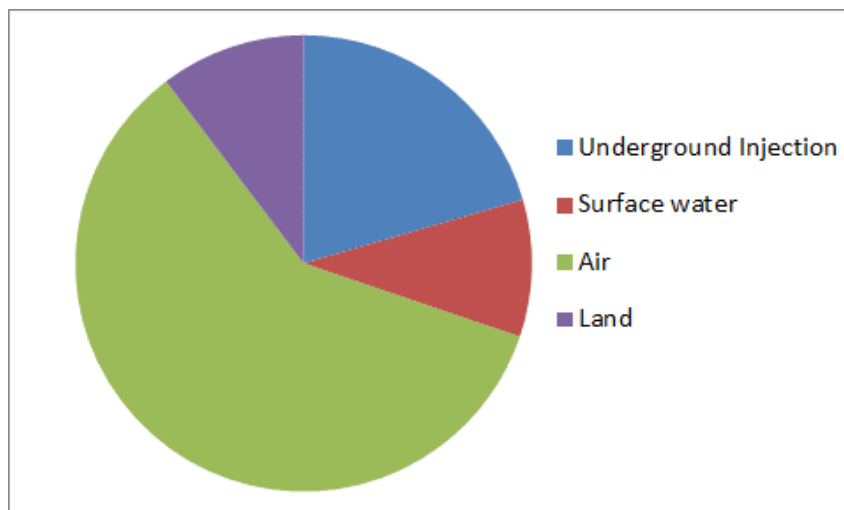


Figure 1. Distribution of Chemical Releases to the Environment

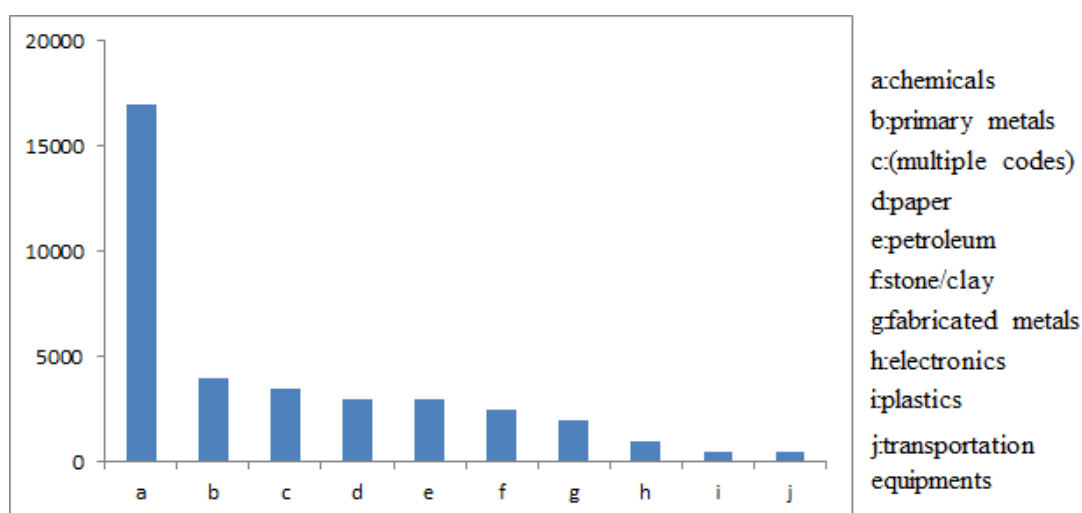


Figure 2. Chemical Releases by Industry Sector (in millions of pounds)

During the 1990s, Paul Anastas proposed the 12 principles of Green Chemistry, still being used today, that depend on the minimization or non-utilization of poisonous solvents in chemical reactions, as well as the non-generation of wastes from these cycles.

1. Waste prevention:-Priorities the minimization of waste at every step
2. Atom economy:-Design the reaction with maximum incorporation of all atoms used in the process into the final product.
3. Less hazardous chemical synthesis:-Design synthetic methods to be as safe as possible (less toxic reactants and products)
4. Designing safer chemicals:-Minimize toxicity by using safer chemicals
5. Safer solvents and auxiliaries:-Choose the safest solvents and auxiliaries available for any given step and use a minimum amount.

6. Design for energy efficiency:- Design the synthetic methods at ambient temperature and pressure
7. Use of Renewable feedstocks:- Whenever technically and economically practicable, use raw materials which are made from renewable sources.
8. Reduce derivatives:- Unnecessary derivatization should be avoided if possible
9. Catalysis:- Use catalytic reagents instead of stoichiometric reagents
10. Design for degradation:- Chemical products should be designed in such a way that degrades and discard easily.
11. Real-time analysis for pollution prevention:-Real-time monitoring of chemical reactions and control before the formation of hazardous substances.
12. Inherently safer chemistry for accident prevention:-Adopt chemical methods that minimize the risk of accidents.

While no reaction can be perfectly 'green', the adverse consequence of the chemical industry can be diminished by implementing these principles of green chemistry wherever possible. These principles help to design environmentally favorable processes from the planning of the product to its synthesis, processing, analysis, its degradation after use.

In 2017, Toxics Release Inventory displays significant reductions in releases of toxic chemicals into the air due to the impact of industrial Green Chemistry practices and the use of preferred waste management systems such as recycling, energy recovery, and treatment.

In conclusion, Green Chemistry is an approach used in the synthesis, processing, and use of chemicals that reduce hazards to human health and the environment. Recently, many innovative chemical reactions have been developed that are efficient, and more environmentally benign. Finally, the success of Green Chemistry ultimately depends on the practicing chemists who will use the same.

References

1. Horvath, I. T.; Anastas, P. T. *Chem. Rev.* **2007**, *107*, 2169
2. U.S. Environmental Protection Agency. Toxics Release Inventory- 1993
<https://nepis.epa.gov/Exe/ZyNET.exe/30006ELS.TXT?ZyActionD=ZyDocument&Client=EPA&Index=1995+Thru+1999&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMont>

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URL

3. P. T. Anastas. *Critical Reviews in Analytical Chemistry*, **1999**, 29, 167-175
4. U.S. Environmental Protection Agency. Toxics Release Inventory (TRI) National Analysis [Internet]. January 2017. <https://www.epa.gov/trinationalanalysis>. 2015 TRI National Analysis

CORROSION AND ITS CONTROL

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The fast-growing industrialization and progress in civilization has demanded the use of metallic objects in different fields. Today it is difficult to imagine the world without metals, as it became an inevitable part of our daily life. Metals exist as such in the earth crust as ores. Metals are extracted from their ores by the application of energy[1, 2]. In the pure metallic state, the metals are unstable as they are considered in higher energy state. So, the reverse process begins and form thermodynamically stable metallic compounds. Hence, when metals are exposed to various corrosive environment, the exposed metal surface begins to decay (conversion to more stable compound). This is the basic reason for metallic corrosion. Although corroded metal is thermodynamically more stable than pure metal but due to corrosion, useful properties of a metal like malleability, ductility, hardness, lustre and electrical conductivity are lost.

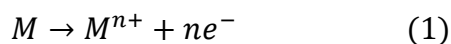
To manage the potential problem of corrosion, it is necessary to understand

1. Mechanism of corrosion
2. Classification of corrosion
3. Methods to prevent corrosion

1. Mechanism of Corrosion

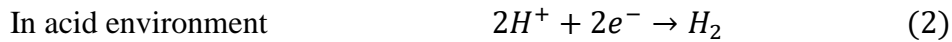
1.1. Electrochemical aspects of corrosion

The basic mechanism of corrosion is the movement of ions at the metal electrolyte interface. The most acceptable electrochemical theory of corrosion is given by Whitney [3-5]. During the aqueous corrosion process, anodic oxidation of the metal and cathodic reduction in the environment creates two interrelated half-cell reactions[6]. For any metal (M) the oxidation reaction at the anodic site is given by

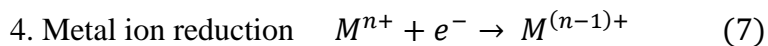
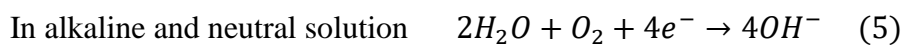
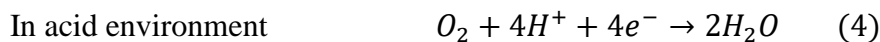


At the cathodic site, the produced electrons react with some reducible components of electrolyte through the following equations

1. Hydrogen evolution



2. Oxygen reduction



According to Faraday's law, the total flow of electrons from the anodic to the cathodic region during the corrosion process generates corrosion current (i_{corr}) and is a measure of the corrosion rate of the metal.

2. Classification of corrosion

Corrosion manifests in different forms. It is desirable to know the form of corrosion since it will help in the identification of the cause of corrosion and in the choice of the most effective method of preventing it. In most corrosion failure analysis, it is necessary to know the form of corrosion, which has been responsible for the failure. Corrosion can be classified in several ways like dry corrosion and wet corrosion or low temperature corrosion and high temperature corrosion etc. Based on the appearance of the corroded metals identified either through visual inspection or using modern spectroscopy there are eight forms of corrosion [7, 8].

2.1. Uniform, or General Corrosion

It is a common type of corrosion that occurs on the entire surface of the metal and causes thinning of the metal and leads to a point of failure. Rusting of iron, high temperature oxidation of metals, and the Fogging of Nickel belongs to this category. This type of corrosion is predictable, controllable, and preventable by applying anti-corrosive coatings, inhibitors, or cathodic protection. So, it is considered a safe form of corrosion. Based on the

corrosion rate of uniform corrosion in millimeter penetration per year (mm/y), metals can be classified into three groups

- A. <0.15 mm/y- Metals in this group have good corrosion resistance and are appropriate for critical parts like springs, valve seats, and pump shafts, etc
- B. 0.15 to 1.5 mm/y- Metals in this category are satisfactory and can be used for valves, tanks, and piping
- C. >1.5 mm/y- Metals belongs to this category are usually not suitable for application

2.2. Localised Corrosion

It occurs at a specific part of a structure. It is more dangerous, difficult to detect, and tends to cause the unexpected failure of structures. Localised corrosion can be further classified as

2.3. Pitting Corrosion

It is extremely localised and generates small pits and cavities on the metal surface due to coating failure or mechanical discontinuities. The pit area becomes anodic and the rest of the metal develops a cathodic region. The small size of pits and accumulation of corrosive products on the pits causes difficulty to predict pitting corrosion quantitatively. Pitting causes weight loss of metal and leads to complete failure of the structure.

2.4. Crevice corrosion

Crevice or contact corrosion occurs at the metal surface or adjacent to the gap or crevice between two joining surfaces. It is usually associated with a small volume of stagnant solution on the microenvironmental level and occurs under gaskets, washers, surface deposits, rivets, and bolts, etc. The development of crevice depends upon various factors like pH, the concentration of oxygen, and constituents. Since the pH and concentration of oxygen are quite low inside the crevice compared to bulk solution, an electrochemical cell set up with anodic metal oxidation in the crevice and cathodic oxygen reduction develop a passive hydroxide layer at the mouth of the crevice and further propagation mechanism of corrosion takes place[9].

2.5. Galvanic corrosion

Also known as bimetallic corrosion and occurs when two electrochemically different metals are in physical contact with the electrolyte, the less noble metal act as anode and tend to corrode faster and the noble metal act as a cathode and corrodes at a slower rate. The effect of galvanic corrosion can be minimised by selecting metals close to each other in the electro potential series.

2.6. Erosion corrosion

Erosion is the removal of metal by the movement of corrosive fluids against the metal surface. The combination of erosion and corrosion creates aggressive pitting on the metal substrate and increases the rate of deterioration. The abrasive particles in the moving fluid cause the depletion of the outer layer. The rate of erosion-corrosion depends upon the physical condition and velocity of the fluid. It is characterized by the appearance of rounded holes, grooves, waves, and typically shows a directional design [10].

2.7. Intergranular corrosion

This type of corrosion occurs by the formation of precipitate and segregates in the specific region of grain boundaries or adjacent to grain boundaries, causing selective dissolution of grain boundaries and affect the mechanical properties of the metal [11].

2.8. Stress corrosion cracking (SCC).

It refers to cracking caused by the repeated presence of tensile stress in a corrosive environment and leads to sudden failure of the structure. SCC is caused either by external stress or residual stress inside the material

2.9. Fatigue corrosion

It is a special type of stress corrosion caused by the combined effects of cyclic stress and a corrosive environment. It generally occurs at surface irregularities or pits.

3. Methods to prevent corrosion

Corrosion never stops but its severity can be controlled by various methods either by elimination of any one of the components of electrochemical cells which accelerates the corrosion process or by isolating the metal from the aggressive environment. The different strategies to prevent corrosion of a metals are anodic or cathodic protection, corrosion inhibitors, and corrosion resistant coating.

3.1. Anodic or Cathodic Protection

Anodic protection is based on the formation of a protective film on metals by externally applied anodic currents and Cathodic protection is a technique used to control the corrosion of a metal surface by making it the cathode of an electrochemical cell.

3.2. Corrosion resistant coatings

Corrosion protection by coating has attracted much attention due to its high efficiency and durability in various aggressive environments. An effective coating must have adhesion with the metal substrate, intrinsic durability, and keep its appearance when subjected to stress, swell, or weathering. Coatings can be classified into noble, sacrificial, metallic, inorganic, organic, and organic-inorganic hybrids (OIHs). Metal coatings are applied by

electro deposition, flame spraying, hot dipping, vapour deposition, etc. Inorganic coatings are applied or formed by spraying, diffusion, or chemical conversion. Inorganic coatings include ceramic coating, cement, silicate, ceramics, conversion coating, and sol-gel coatings. OIHs offer an effective coating on the metal substrate by linking both inorganic and organic phases covalently on the molecular scale. OIHs coating developed by sol-gel process is considered as an effective alternative to Chromate conversion coatings for the metallic substrate.

3.3. Corrosion Inhibitors

Acid solutions are extensively used in industry, the most important of which are industrial acid cleaning, acid de-scaling, acid pickling, and oil well acidizing[12, 13]. Corrosion inhibitors are usually used to minimize the corrosive attack of metallic materials by different aggressive media. An efficient inhibitor should be economical, environment friendly, and inhibit the corrosion process when present in a small concentration[14]. Corrosion inhibitors can be classified into vapor phase, liquid phase, and environmental conditioners. The inhibitor interacts with the metal surface and forms an inhibitive surface film at the metal/electrolyte interface[15, 16]. Liquid phase inhibitors are classified as cathodic, anodic, or mixed type inhibitors, based on whether they inhibit the anodic, cathodic, or both the electrochemical corrosion process. Anodic inhibitors develop a protective oxide film on the surface of the metal and causing a large anodic corrosion potential shift and thereby force the metal surface into the passivation region and hence commonly referred to as passivators. Cathodic inhibitors inhibit the corrosion process by either decreasing the cathodic reduction rate or by selectively precipitating an insoluble species onto the cathodic sites to limit the diffusion of reducing species to the metal surface. Mixed (adsorption) inhibitors work by reducing the anodic and cathodic corrosion reactions[17].

References

- [1] J.R. Davis, Corrosion: Understanding the basics, Asm International, 2000.
- [2] H.H. Hassan, E. Abdelghani, M.A. Amin, Inhibition of mild steel corrosion in hydrochloric acid solution by triazole derivatives: Part I. Polarization and EIS studies, *Electrochimica Acta*, 52 (2007) 6359-6366.
- [3] N. Sato, 1989 Whitney Award Lecture: toward a more fundamental understanding of corrosion processes, *Corrosion*, 45 (1989) 354-368.
- [4] W. Whitney, The Corrosion of Iron, *Corrosion*, 3 (1947) 331-340.
- [5] O.P. Watts, The electrochemical theory of corrosion, *Transactions of the Electrochemical Society*, 64 (1933) 125.

- [6] E. Bardal, Corrosion and protection, Springer Science & Business Media, 2007.
- [7] M.G. Fontana, Corrosion engineering, Tata McGraw-Hill Education, 2005.
- [8] N. Perez, Electrochemistry and corrosion science, Springer, 2004.
- [9] J. Oldfield, W. Sutton, Crevice corrosion of stainless steels: i. a mathematical model, *British corrosion journal*, 13 (1978) 13-22.
- [10] S. Rajahram, T. Harvey, R. Wood, Erosion–corrosion resistance of engineering materials in various test conditions, *Wear*, 267 (2009) 244-254.
- [11] J. Galvele, S. de De Micheli, Mechanism of intergranular corrosion of Al-Cu alloys, *Corrosion science*, 10 (1970) 795-807.
- [12] S.A. Umoren, M.M. Solomon, I.B. Obot, R.K. Suleiman, A critical review on the recent studies on plant biomaterials as corrosion inhibitors for industrial metals, *Journal of Industrial and Engineering Chemistry*, 76 (2019) 91-115.
- [13] M. Al-Otaibi, A. Al-Mayouf, M. Khan, A. Mousa, S. Al-Mazroa, H. Alkhatlan, Corrosion inhibitory action of some plant extracts on the corrosion of mild steel in acidic media, *Arabian Journal of Chemistry*, 7 (2014) 340-346.
- [14] R.Y. Khaled, A. Abdel-Gaber, H. Holail, Electrochemical studies of the inhibition effect of 4, 6-dichloro-2-(methylthio) pyrimidine on the corrosion of AISI type 321 stainless steel in 1.0 M hydrochloric acid, *Int. J. Electrochem. Sci*, 11 (2016) 2790-2798.
- [15] V.S. Sastri, Green corrosion inhibitors: theory and practice, John Wiley & Sons, 2012.
- [16] A. Rostami, Review and evaluation of corrosion inhibitors used in well stimulation, in: SPE International Symposium on Oilfield Chemistry, OnePetro, 2009.
- [17] E. Gutiérrez, J.A. Rodríguez, J. Cruz-Borbolla, J.G. Alvarado-Rodríguez, P. Thangarasu, Development of a predictive model for corrosion inhibition of carbon steel by imidazole and benzimidazole derivatives, *Corrosion Science*, 108 (2016) 23-35.

SUSTAINABLE POLYMERS AND THEIR COMPOSITES AS A FUTURE CHALLENGE

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The demand for plastics has been increased remarkably in the last few decades and environmental pollution causing these materials has become one of the most important concerns of the ecosystem. Most of the conventional polymers are highly persistent in the environment though they are obtained from fossil fuels and show, which is the main pollutant and there arise sustainability issues like petroleum depletion and waste management. Nowadays researchers are forced to manufacture environmentally friendly and recyclable plastic materials and their composites. By considering the applications of these materials in food packaging and other sectors such as agriculture, pharmaceuticals, biomedicine, etc researchers are looking for fast-growing technologies in order to develop sustainable materials.

A sustainable polymer is a plastic material that addresses the needs of consumers without damaging our environment, health, and economy. To do this, researchers are working to develop polymers that, when compared with their non-sustainable counterparts: use renewable feedstocks, such as plants, for production use less net water and non-renewable energy in production emit fewer greenhouse gases during production produce less waste in production has a smaller carbon-footprint have a facile end life.

In the case of traditional polymers chemicals derived from petroleum or natural gases are taken as monomers, these monomers are used to produce plastic materials and these plastic products can be recycled, incinerated, or simply thrown away. While monomers in sustainable polymers are plant origin, these plant-originated monomers may be obtained by fermenting plants, simple extraction, bioengineering, microbial pathways, etc. thus obtained renewable chemicals are converted into plastic products. These sustainable plastics are easily compostable instead of recycle or incinerated. The most important commercially available sustainable polymer is PLA which cannot be recycled currently. But sustainable polymers are designed to use for a long time without any damage, i.e. they will never degrade if you use them properly or by putting them on your shelf. In order to degrade it properly so many

conditions should be satisfied, they will not biodegrade in a landfill due to low temperature and lack of oxygen, etc. they will also not undergo degradation above the ground, so we have to provide sufficient conditions or should always dispose of it properly.

There is a question that whether sustainable polymers are compostable or not, the answer is of course “Yes”, while compared to petroleum-based polymers sustainable polymers are more environmentally friendly. This means that they would produce less pollution, less non-renewable energy to make, etc. nowadays sustainable polymers are a growing segment in the industry, the main area of sustainable polymer industry include polylactide which is derived from corn is made into plastic cutlery, cloth fibers, food containers, surprisingly in cell phone cases, etc. seating cushions and some foam pillows are manufactured using polyurethane which is modified soybean oil. Thus, the list of such innovative products will grow exponentially in the research field. There are many challenges to sustainable polymers such as elasticity, toughness, color, melting temperature, etc. so universities and companies are in extensive research on improving the physical properties discussed above.

Unfortunately, there is no easy way to identify the product whether it is made from conventional polymers or from sustainable polymers. This means there isn't any universally accepted definition of sustainable with respect to the product. But there are some certifications for compostability and biological content which can help you to identify which products are truly more environmentally friendly. Commonly used sustainable polymers are obtained from plants like sugarcane, seed oils, vegetable oils, corn, etc, the scientists around the world-famous universities are in a search of finding or making non-food sources like trees, agricultural waste, grass, etc. these research studies in the present era can reveal the exact potential of sustainable polymers and their applications in the various fields. It is a big expectation for common people that the researchers will contribute innovative products like renewable and biodegradable food packaging materials in order to avoid conventional polymers and thus reduce environmental pollution.

Conclusion

Due to the biodegradability and enhanced mechanical properties, sustainable/biodegradable polymers have great potential in the industry. So instead of products manufactured from sustainable polymers, we have to use their composites. By

mixing different fillers with these polymers. The composites may have vast advantages like processability, heat resistance, weather resistance, low cost, abrasion, and chemical resistance. New innovations led technology to enhance the above characteristics and production capacity of sustainable polymers. The sharp rise in global oil prices, growing concerns over the depletion of non-renewable raw materials, and global interest in sustainability, responsible packaging production, and efficient waste management have created a remarkable interest in the designing of crop-based packaging materials.

References

1. O. Olabisi and K. P. Adewale, *Handbook of Thermoplastics*, CRC Press, 2nd edition, 2015, <http://www.loc.gov/catdir/enhancements/fy0647/97000058-d.html>.
2. Y. Zhu, C. Romain, and C. K. Williams, “Sustainable polymers from renewable resources,” *Nature*, vol. 540, no. 7633, pp. 354–362, 2016. View at: [Publisher Site](#) | [Google Scholar](#)
3. M. Baiardo, G. Frisoni, M. Scandola et al., “Thermal and mechanical properties of plasticized poly(L-lactic acid),” *Journal of Applied Polymer Science*, vol. 90, no. 7, pp. 1731–1738, 2003. View at: [Publisher Site](#) | [Google Scholar](#)
4. A. Ashori, “Wood–plastic composites as promising green-composites for automotive industries!,” *Bioresource Technology*, vol. 99, no. 11, pp. 4661–4667, 2008. View at: [Publisher Site](#) | [Google Scholar](#)
5. M. Valente and A. Quitadamo, “Polymeric matrix composites at reduced environmental impact,” *Polymer Engineering & Science*, vol. 57, no. 7, pp. 651–656, 2017. View at: [Publisher Site](#) | [Google Scholar](#)

EXPLORING THE APPLICATIONS OF “CLICK CHEMISTRY”

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*PG Department of Chemistry, KAHM Unity Women's College, Manjeri,**Narukara (PO), Malappuram (Dt), Kerala, Pin: 676122**E-mail: thasnim6390@gmail.com***Abstract**

Mimicking natural biochemical processes, click chemistry is a modular approach to organic synthesis, joining together small chemical units quickly, efficiently and predictably. In contrast to complex traditional synthesis, click reactions offer high selectivity and yields, near-perfect reliability and exceptional tolerance towards a wide range of functional groups and reaction conditions. These 'spring loaded' reactions are achieved by using a high thermodynamic driving force, and are attracting tremendous attention throughout the chemical community. Originally introduced with the focus on drug discovery, the concept has been successfully applied to materials science, polymer chemistry and biotechnology.

Introduction

The term “Click Chemistry” was introduced by Sharpless *et al.* in 2001 to describe chemistry tailored to generate substances quickly and reliably by selectively joining (“click”) small units together similar to the modular strategies adopted by Nature.¹ These authors suggested a set of requirements to be fulfilled by a reaction to classify it as a ‘Click’ reaction.¹ The main goal was to encourage synthetic chemists to focus more on the production of arrays of simple molecules with the same properties available in complex natural molecules by making use of carbon-carbon and carbon-hetero atom bond formations in a much simpler way similar to Nature’s synthetic strategy.¹ Click reactions are modular reactions with wide scope, high product selectivity and high thermodynamic driving force, usually greater than 20 kcal mol⁻¹. Such “spring-loaded” reactions proceed rapidly to completion and also tend to be highly selective towards the formation of a single product. Generally, Click reactions are room temperature reactions based on readily available starting

materials and benign solvents, yielding near quantitative amount of products via simple and non-chromatographic separation methods.

Among the various reactions that are fulfilling the Click criteria, the [3+2]azide-alkyne cycloaddition (Huisgen cycloaddition) is now emerged as an established tool in modern medicinal chemistry.² Azide and alkyne functionalities can be readily introduced and have a high tolerance for various other functional groups and have enough kinetic stability.³ Since the work presented in the upcoming chapters are on the use of Copper (I) catalyzed the [3+2]azide-alkyne cycloaddition for the development of multipurpose small molecules for medicinal and materials applications, the focus of this review has been restricted to 1,3-dipolar click cycloadditions.

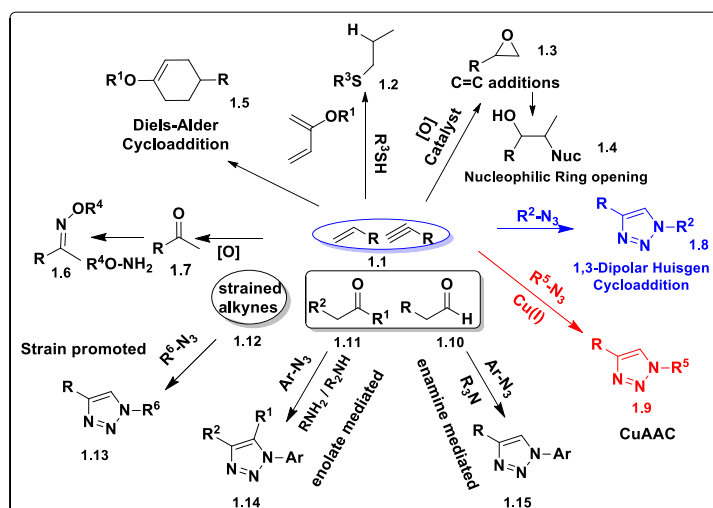
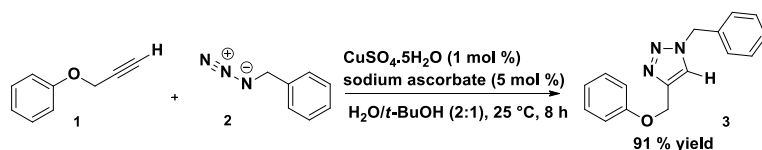


Figure 1: Classification of Click reactions

1,3 -Dipolar Cycloadditions and CuAAC

The 1,3-dipolar cycloaddition is a chemical reaction between a 1,3-dipole and a dipolarophile to form a five-membered ring. In 1960s, Huisgen recognized this type of reaction for its generality, scope and mechanism by Huisgen, and he coined the term 1,3-dipolar cycloaddition.⁴ Hence, the reaction is sometimes referred to as the Huisgen cycloaddition. Unfortunately, the thermal Huisgen 1,3-Dipolar cycloaddition of alkynes to azides requires high temperatures and often produces mixtures of the 1,4- and 1,5-disubstituted 1,2,3-triazoles when using asymmetric alkynes.⁵ A copper-catalyzed variation of Huisgen's azide-alkyne cycloaddition (CuAAC reaction) was reported by the groups of Meldal and Sharpless independently in 2002.⁶ This reaction fits the "click chemistry" concept

well because a close examination of the azide-alkyne cycloaddition shows that it fulfills many of the prerequisites of click concept.



Scheme 1. Example for CuAAC reaction of benzyl azide with (prop-2-yn-1-yloxy)benzene

This reaction is applicable to a wide variety of substrates with various functional groups and the catalytic process is insensitive towards the presence of air and pH changes in a solvent mixture of water and *t*-BuOH. This strictly regioselective stepwise process selectively produce 1,4-disubstituted 1,2,3-triazole only and accelerates the reaction by a factor of up to 10^7 in comparison to Huisgen's thermal procedure.⁷ In addition to this, since large number of monosubstituted alkynes and organic azides are commercially available and many others can easily be synthesized with a wide range of functional groups, it is easy to make large library of 1,2,3-triazoles derivatives for screening purpose.

Applications of Click Chemistry (CUAAC)

The popularity of the CuAAC is largely a result of the unique properties of both azides and the resulting triazoles.⁸ The combination of the robustness of the triazole bond, the resemblance to an amide bond, and the potential biological properties it could endow make the triazole linkage not merely a benign, easily synthesized linker, but an integral part of the success of click chemistry. In addition to this, the simplicity, reliability and the bioorthogonality of the starting materials has made the CuAAC reaction an asset to a hugely varied range of scientific applications. The wide scope of CuAAC is firmly demonstrated by the use in different areas of life and material sciences such as drug discovery,⁹ bioconjugation,¹⁰ polymer and materials science,¹¹ including supramolecular chemistry,¹² DNA labeling¹³ and oligonucleotide synthesis,¹⁴ assembly of glycoclusters¹⁵ and glycodendrimers,¹⁶ preparation of stationary phases for HPLC column,¹⁷ development of microcontact printing,¹⁸ conjugation of molecular cargos to the headgroup of phospholipids,¹⁹ and construction of bolaamphiphilic structures²⁰ are a further examples of the use of CuAAC. It would be impossible to give a complete overview of the numerous applications of the CuAAC. For our purposes, the applications of 'click' chemistry have been summarized with

illustrative examples in various categories; applications in materials science, for radiolabelling, for bioconjugation, and in drug discovery.

a) Material Science

The value of click chemistry for materials synthesis possibly becomes most apparent in the area of material chemistry. Several recent reviews have described the use of CuAAC for the synthesis of macromolecular structures like dendritic, branched, linear and cyclic copolymers.²¹ Triazole-based dendrons can be divergently synthesized via CuAAC reaction. These dendrons were then anchored to a variety of polyacetylene cores to generate dendrimers. Since then, the CuAAC reaction has been widely employed to synthesize or modify various dendrimers.²² A click chemistry based dendrimer **4** is shown in Figure 2.

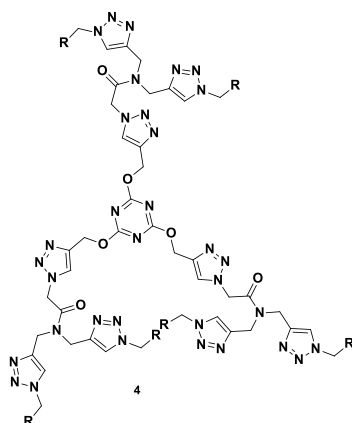


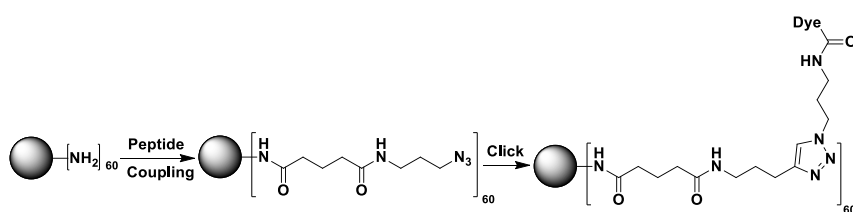
Figure 2. ‘Click’ chemistry based dendrimers

b) Bioconjugation

Bioconjugation is the process by which synthetic molecules are attached to biological targets or by which biomolecules are linked together. It involves attachment of synthetic labels to biomolecular building blocks, such as fusing two or more proteins together or linking a carbohydrate with a peptide, and covers a wide range of science between molecular biology and chemistry. The possibility of applying click chemistry in bioconjugation was first demonstrated by Meldal *et al* for the preparation of peptidotriazoles *via* solid state synthesis.^{6a} Their goal was to develop new and more efficient synthetic methods to prepare various [1,2,3]-triazole pharmacophores for potential biological targets. This initial report made

possible the introduction of various novel functional and reporter groups into biomolecules such as peptides and proteins,²³ for DNA labeling and modification,²⁴ and for cell surface labeling.²⁵

Finn and co-workers successfully labeled Cowpea mosaic virus particles (CPMV) with fluorescein with >95% yield.²⁶ Similarly, Tirrell and Link were able to modify *Escherichia coli* with an azide-bearing outer membrane protein C(OmpC). Schultz *et al* developed a method to genetically-encode proteins of *Saccharomyces cerevisiae* with azide- or acetylene-based synthetic amino acids.²⁷ The genetic modification was done by reacting an alkyne or an azide bearing protein with the counterpart unnatural amino acid. Click chemistry continues to attract attention for labeling of proteins and live organisms.



Scheme 2. Labelling of virus capsids by CuAAC

c) Radiochemistry

The CuAAC is an ideal ligation reaction for radiolabeling sensitive biomolecules. Alkyne or azide derivatives of radioisotope containing compounds could be used for labeling biomolecules such as folic acid, peptides, proteins, and glycopeptides. For example, an ¹¹C isotope label was introduced via converting [¹¹C]-CH₃I into [¹¹C]-CH₃N₃ by nucleophilic substitution and subsequently reacting the azide with an alkyne-modified peptide. ¹⁸F labeling for PET imaging was achieved by clicking azidomethyl-4-[¹⁸F]-fluorobenzene to a modified peptide.²⁸ CuAAC ligations have a significant impact on the synthesis and development of radiopharmaceuticals and it has vast application in the preparation of imaging agents for SPECT and PET, including small molecules, peptides, and proteins labeled with radionuclides such as ¹⁸F, ⁶⁴Cu, and ¹¹¹In.²⁹ Various researchers have shown that CuAAC is a great approach for the construction of radiotracers also.

d) Drug Discovery

In history and even now a days, lead discovery and optimization had aided by combinatorial methods and high throughput screening to generate library of test compounds

for screening. However, due to unreliability and new discoveries revealed click chemistry as a modular for the synthesis of drug-like molecules that can accelerate the drug discovery process by utilizing a few practical and reliable reactions. It is a new type of chemistry that able to synthesize complex molecule in an efficient manner.¹It makes use of few chemical reactions for the synthesis and designing of new building blocks. Drug discovery based on Natures secondary metabolites is very slow and complex synthesis and thereby, click chemistry provides faster lead discovery and optimization.¹

This commendably straightforward chemistry, which can be conducted in aqueous media, has been widely applied as a powerful tool for theselective modifications of enzymes³⁰ viruses³¹and cells.³² Among the best-known examples of triazole-containing structures is, a β -lactamase inhibitor which is marketed in combination with the broad spectrum antibiotic piperacillin. Indeed, when first described, tazobactam and related triazole-containing compounds (**5**, Figure 3) turned out to be potent β -lactamase inhibitors with higher potency than clavulanic acid and sulbactam, and the triazole ring appears to play a pivotal role for its potency.³³ In the antibiotics field, triazoles have been also used to improve pharmacokinetic properties of the desired drug. For example, cephalosporins endowed with good oral availability were obtained linking the triazoles moiety to the cephalosporin core (**6**, Figure 3).³⁴Indeed; it is not just antibiotics which benefit from the triazole ring.

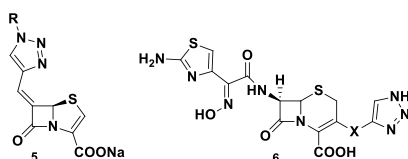


Figure 3. Example of β -lactamase inhibitors incorporating the 1,2,3-triazole moiety

Click chemistry, due to its highly modular and efficient reaction nature, has been identified as one of the most practical methods toward fragment-based enzyme inhibitor development. Using fragment pro-inhibitor library screening and click chemistry reaction, researchers developed a large class library of efficient enzyme inhibitors of various enzymes such as Protein Tyrosine Phosphatase Inhibitors, Protein Kinase Inhibitors, Transferase Inhibitors, Glycogen Phosphorylase Inhibitors, Serine Hydrolase Inhibitors, Metalloproteinase Inhibitors, Aspartic Protease Inhibitors, Oxidoreductase Inhibitors and Glycosidase Inhibitors etc.³⁵

Click Derived Cancer Growth Inhibitors

Chemotherapy is considered as the most effective method among many other methods prevalent to treat cancer. Several nucleoside drugs have been developed as cancer treatment agents: cladribine, clofarabine, capecitabine, cytarabine, fludarabine, gemcitabine, decitabine, and floxuridine.³⁶ The development of new therapeutic approach to breast cancer remains one of the most challenging areas in cancer research. Inhibitors of cyclin-dependent kinases (CDKs) are an emerging class of drugs for the treatment of breast cancers. Experimental evidence suggests that CDK inhibitors inhibit the cyclin D-dependent kinase activity and thus prevent tumor growth and/or at least partially revert the transformed phenotype. Several compounds are currently in clinical trials including flavopiridol (**7**), R-roscovitine (CYC202) (**8**), BMS-387032 (**9**), and UCN-01 (7-hydroxystaurosporine) (**10**).³⁷ CDK inhibitors are currently under evaluation in clinical trials as single agents and as sensitizers in combination with radiation therapy and chemotherapies.

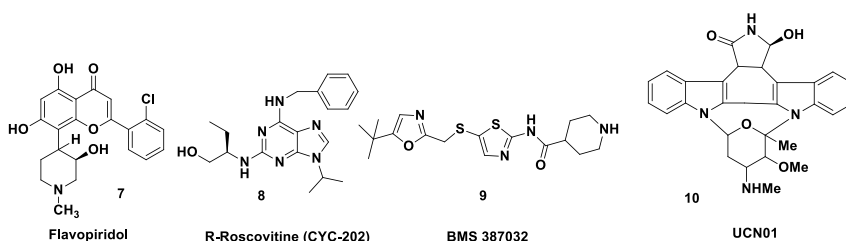


Figure 6. CDK inhibitors under clinical trials

Conclusions

In conclusion, this review summarizes the growing application of “click” chemistry in diverse areas such as bioconjugation, drug discovery, materials science, and radiochemistry. Click chemistry has found increasing applications in all aspects of drug discovery in medicinal chemistry, such as for generating lead compounds through combinatorial methods. Bioconjugation via click chemistry is rigorously employed in proteomics and nucleic acid research. In radiochemistry, selective radiolabeling of biomolecules in cells and living organisms for imaging and therapy has been realized by this technology.

Click chemistry has proven itself to be superior in satisfying many criteria, thus, one can expect it will consequently become a more routine strategy in the near future for a wide range of applications since it links various types of chemistry with biology and can tailor various useful syntheses in future.

References

- (1) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2001**, *40*, 2004-2021.
- (2) (a) Huisgen, R. *Pure Appl. Chem.* **1989**, *61*, 613-628. (b) Huisgen, R.; Szeimies, G.; Moebius, L. *Chem. Ber.* **1967**, *100*, 2494-2507.
- (3) Bock, V. D.; Hiemstra, H.; Van Maarseveen, J. H. *Eur. J. Org. Chem.* **2006**, 51-68.
- (4) (a) Huisgen, R. *Proc Chem Soc, London.* **1961**, 357-396. (b) Huisgen, R. *Angew Chem.* **1963**, *75*, 604-637. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565-598. (c) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 633-645.
- (5) (a) Huisgen, R. *1,3-Dipolar Cycloaddition Chemistry* (Ed.: A. Padwa), Wiley, New York, **1984**, 1-176. (b) Bastide, J.; Henri-Rousseau, O. *Bull. Chim. Soc. Fr.* **1973**, 2294-2296. (c) Clarke, D.; Mares, R. W.; McNab, H. *J. Chem. Soc. Perkin. Trans.* **1997**, *1*, 1799-1804.
- (6) (a) Tornøe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057-3064. (b) Rostovtsev, V.V.; Green, L.G.; Fokin, V.V.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2002**, *41*, 2596-2599.
- (7) (a) Himo, F.; Lovell, T.; Hilgraf, R.; Rostovtsev, V. V.; Noodleman, L.; Sharpless, K. B.; Fokin, V. V. *J Am Chem Soc.* **2005**, *127*, 210-216. (b) Hein, J. E.; Fokin, V.V. *Chem Soc Rev.* **2010**, *39*, 1302-1315.
- (8) (a) Roper, S.; Kolb, H. C. *Wiley-VCH: Weinheim*, **2006**, *34*, 313-339. (b) Sharpless, K. B.; Manetsch, R. *Expert Opin. Drug Discovery.* **2006**, *1*, 525-538. (c) Tron, G. C.; Pirali, T.; Billington, R. A.; Canonico, P. L.; Sorba, G.; Genazzani, A. A. *Med. Res. Rev.* **2008**, *28*, 278-308.
- (9) Alvarez, R.; Velazquez, S.; San-Felix, A.; Aquaro, S.; De Clercq, E.; Perno, C.-F.; Karlsson, A.; Balzarini, J.; Camarasa, M. J. *J. Med. Chem.* **1994**, *37*, 4185-4194.
- (10) (a) Pieters, R. J.; Rijkers, D. T. S.; Liskamp, R. M. J. *QSAR Comb. Sci* **2007**, *26*, 1181-1190. (b) Dirks, A. J.; Cornelissen, J.; van Delft, F. L.; van Hest, J. C. M.;

- Nolte, R. J. M.; Rowan, A. E.; Rutjes, F. *QSAR Comb. Sci.* **2007**, *26*, 1200-1210. (c) Salisbury, C. M.; Cravatt, B. F. *QSAR Comb. Sci.* **2007**, *26*, 1229-1238.
- (11) (a) Binder, W. H.; Kluger, C. *Curr. Org. Chem.* **2006**, *10*, 1791-1815. (b) Nandivada, H.; Jiang, X. W.; Lahann, J. *Adv. Mater.* **2007**, *19*, 2197-2208. (c) Fournier, D.; Hoogenboom, R.; Schubert, U. S. *Chem. Soc. Rev.* **2007**, *36*, 1369-1380. (d) Golas, P. L.; Matyjaszewski, K. *QSAR Comb. Sci.* **2007**, *26*, 1116-1134. (e) Devaraj, N. K.; Collman, J. P. *QSAR Comb. Sci.* **2007**, *26*, 1253.
- (12) (a) Zhou, Z.; Fahrni, C. J. *J. Am. Chem. Soc.* **2004**, *126*, 8862-8863. (b) Link, A. J.; Vink, M. K. S.; Tirrell, D. A. *J. Am. Chem. Soc.* **2004**, *126*, 10598-10602. (c) Lewis, W. G.; Magallon, F. G.; Fokin, V. V.; Finn, M. G. *J. Am. Chem. Soc.* **2004**, *126*, 9152-9153. (d) Sivakumar, K.; Xie, F.; Cash, B. M.; Long, S.; Barnhill, H. N.; Wang, Q. *Org. Lett.* **2004**, *6*, 4603-4606.
- (13) For selected reviews, see: (a) Miljanic, O. S.; Dichtel, W. R.; Aprahamian, I.; Rohde, R. D.; Agnew, H. D.; Heath, J. R.; Stoddart, J. F. *QSAR Comb. Science.* **2007**, *26*, 1165-1174. (b) Aprahamian, I.; Miljanic, O. S.; Dichtel, W. R.; Isoda, K.; Yasuda, T.; Kato, T.; Stoddart, J. F. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1856-1869. (c) Braunschweig, A. B.; Dichtel, W. R.; Miljanic, O. S.; Olson, M. A.; Spruell, J. M.; Khan, S. I.; Heath, J. R.; Stoddart, J. F. *Chem. Asian J.* **2007**, *2*, 634-647. For selected papers see: (d) Aucagne, V.; Haenni, K. D.; Leigh, D. A.; Lusby, P. J.; Walker, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 2186-2187. (e) O'Reilly, R. K.; Joralemon, M. J.; Hawker, C. J.; Wooley, K. L. *Polym. Sci. Polym. Chem.* **2006**, *44*, 5203-5217.
- (14) Gierlich, J.; Burley, G. A.; Gramlich, P. M. E.; Hammond, D. M.; Carell, T. *Org. Lett.* **2006**, *8*, 3639-3642.
- (15) Nuzzi, A.; Massi, A.; Dondoni, A. *QSAR Comb. Sci.* **2007**, *26*, 1191-1199.
- (16) Dondoni, A.; Marra, A. *J. Org. Chem.* **2006**, *71*, 7546-7557 and references therein.
- (17) (a) Joosten, J. A. F.; Tholen, N. T. H.; Ait El Maate, F.; Brouwer, A. J.; van Esse, G. W.; Rijkers, D. T. S.; Liskamp, R. M. J.; Pieters, R. J.; *Eur. J. Org. Chem.* **2005**, 3182-3185. (b) Fernandez-Megia, E.; Correa, J.; Rodri'guez-Meizoso, I.; Riguera, R. *Macromol.* **2006**, *39*, 2113-2120.
- (18) Guo, Z.; Lei, A.; Liang, X.; Xu, Q. *Chem. Commun.* **2006**, 4512-4514.
- (19) Rozkiewicz, D. I.; Janczewski, D.; Verboom, W.; Ravoo, B. J.; Reinhoudt, D. N. *Angew. Chem., Int. Ed.* **2006**, *45*, 5292-5296.

- (20) (a) Musiol, H. –J.; Dong, S.; Kaiser, M.; Bausinger, R.; Zumbusch, A.; Bertsch, U.; Moroder, L. *ChemBioChem*. **2005**, *6*, 625-628. (b) Cavalli, S.; Tipton, A. R.; Overhand, M.; Kros, A.; *Chem. Commun.* **2006**, 3193-3195. (c) Hassane, F. S.; Frisch, B.; Schuber, F. *Bioconjugate Chem.* **2006**, *17*, 849-854.
- (21) (a) Franc, G.; Kakkar, A. K. *Chem. Soc. Rev.* 2010, *39*, 1536–1544. (b) Gao, C.; Yan, D. *Prog. Polym. Sci.* **2004**, *29*, 183–275. (c) Tang, B.Z. *Chem. Soc. Rev.* **2010**, *39*, 2522–2544. (d) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747–3792.
- (22) (a) Wu, P. *et al.* *Chem. Commun.* **2005**, 5775–5777. (b) Joralemon, M.J. *et al.* *Macromolecules*, **2005**, *38*, 5436–5443.
- (23) Baskin, J. M.; Bertozzi, C. R. *QSAR. Comb. Sci.* **2007**, *26*, 1211.
- (24) (a) Chevolut, Y.; Bouillon, C.; Vidal, S.; Morvan, F.; Meyer, A.; Cloarec, J. P.; Jochum, A.; Praly, J. P.; Vasseur, J. J.; Souteyrand, E. *Angew. Chem. Int. Ed.* **2007**, *46*, 2398. (b) Weisbrod, S. H.; Marx, A. *Chem. Commun.* **2008**, 5675. (c) Gramlich, P. M. E.; Warncke, S.; Gierlich, J.; Carell, T. *Angew. Chem. Int. Ed.* **2008**, *47*, 3442.
- (25) Link, A. J.; Tirrell, D. A. *J. Am. Chem. Soc.* **2003**, *125*, 11164.
- (26) Wang, Q.; Chan, T. R.; Hilgraf, R.; Fokin, V. V.; Sharpless, K. B.; Finn, M. G. *J. Am. Chem. Soc.* **2003**, *125*, 3192-3193.
- (27) Deiters, A.; Cropp, T. A.; Mukherji, M.; Chin, J. W.; Anderson, J. C.; Schultz, P. G. *J. Am. Chem. Soc.* **2003**, *125*, 11782.
- (28) Carroll, L.; Boldon, S.; Bejot, R.; Moore, J. E.; Declerck, J.; Gouverneur V. *Org. Biomol. Chem.* **2011**, *9*, 136- 140.
- (29) Dexing, Z.; Brian, M.Z.; Jason, S. L.; and Carolyn, J. A. *J. Nucl. Med.* **2013**, *54*, 829–832.
- (30) Schultz, P. G. *J. Am. Chem. Soc.* **2003**, *125*, 11782-11783.
- (31) (a) Wang, Q.; Chan, T. R.; Hilgraf, R.; Fokin, V. V.; Sharpless, K. B.; Finn, M. G. *J. Am. Chem. Soc.* **2003**, *125*, 3192–3193. (b) Gupta, S. S.; Kuzelka, J.; Singh, P.; Lewis, W. G.; Manchester, M.; Finn, M. G. *Bioconjugate. Chem.* **2005**, *16*, 1572-1579. (c) Gupta, S. S.; Raja, K. S.; Kaltgrad, E.; Strable, E.; Finn, M. G. *Chem. Commun.* **2005**, 4315-4317
- (32) Link, A. J.; Vink, M. K. S.; Tirrell, D. A. *J. Am. Chem. Soc.* **2004**, *126*, 10598-10602.
- (33) (a) Bennett, I. S.; Brooks, G.; Broom, N. P.; Calvert, S. H.; Coleman, K.; Francois, I. *J. Antibiot.* **1991**, *44*, 969–977. (b) Bennett, I. S.; Broom, N. P.; Bruton, G.; Calvert,

- S.; Clarke, B. P.; Coleman, K.; Edmondson, R.; Edwards, P.; Jones, D.; Osborne, N. F.; Walker, G. *J. Antibiot.* **1991**, *44*, 331–337.
- (34) Kume, M.; Kubota, T.; Kimura, Y.; Nakashimizu, H.; Motokawa, K.; Nakano, M. *J. Antibiot.* **1993**, *46*, 177–192.
- (35) Prakasam, T.; Dariusz, M.; Krzysztof, J. *Chem. Rev.* **2013**, *113*, 4905–4979 and references therein.
- (36) (a) Lauria, F.; Benfenati, D.; Raspadori, D.; Rondelli, D.; Zinzani, P. L.; Tura, S. *Leuk. Lymphoma.* **1993**, *11*, 399. (b) Pui, C. H.; Jeha, S.; Kirkpatrick, P. *Nat. Rev. Drug Disc.* **2005**, *4*, 369. (c) Bonate, P. L.; Arthaud, L.; Cantrell, W. R.; Stephenson, K.; Secrist, J. A.; Weitman, S. *Nat. Rev. Drug Disc.* **2006**, *5*, 855; (d) Issa, J.-P.; Kantarjian, H.; Kirkpatrick, P. *Nat. Rev. Drug Disc.* **2005**, *4*, 275. (e) Gore, S. D.; Jones, C.; Kirkpatrick, P. *Nat. Rev. Drug Disc.* **2006**, *5*, 891.
- (37) Benson, C.; Kaye, S.; Workman, P.; Garrett, M.; Walton, M.; De Bono, J. *British Journal of Cancer.* **2005**, *92*, 7 – 12.