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Contact
Publisher: Atatürk University
Address: Atatürk University, Yakutiye, Erzurum, Türkiye

Publishing Service: AVES
Address: Büyükdere Cad. 199/6, 34394, Şişli, İstanbul, Türkiye
Phone: +90 212 217 17 00
E-mail: info@avesyayincilik.com
Webpage: www.avesyayincilik.com

NanoEra

AIMS AND SCOPE

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NanoEra aims to contribute to the literature by publishing manuscripts at the highest scientific level in the fields of nanoscience and nanoengineering. The journal publishes original articles and reviews that are prepared in accordance with ethical guidelines.

The scope of the journal is all fields that are directly or indirectly related to research on the design, characterization, fabrication, and applications of structures, devices, and systems involving the manipulation or control of atomic, molecular, and nanoscale materials, and events.

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Editor in Chief: Hayrunnisa NADAROĞLU
Address: Atatürk University, Vocational School of Technical Sciences & Nanoscience and Nanoengineering Research and Application Center, Erzurum, Türkiye
E-mail: hnisa25@atauni.edu.tr

Publisher: Atatürk University
Address: Atatürk University, Yakutiye, Erzurum, Türkiye

Publishing Service: AVES
Address: Büyükdere Cad., 199/6, 34394 Şişli, İstanbul, Türkiye
Phone: +90 212 217 17 00
E-mail: info@avesyayincilik.com
Webpage: www.avesyayincilik.com

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Nanotechnology and the Construction Industry

Terlumun UTSEV[1]
Michael TORYILA TIZA[2]
Emmanuel OGUNLEYE[3]
Terlumun SESUGH[3]
Victoria Hassana JIYA[4]
Collins ONUZULIKE[4]

[1]Department of Civil Engineering, Joseph Sarwuan Tarka University
[2]Department of Civil Engineering, University of Nigeria
[3]Emmanesta Construction and Engineering Limited, Iwaro Central
[4]Department of Civil and Environmental Engineering, Air Force Institute of Technology

ABSTRACT

Different industries are pursuing nanotechnology research and product development with aggressiveness, including the medical field and those that manufacture cutting-edge materials and semiconductors. However, while the benefits and barriers to entry of research and development have been widely studied, few studies have examined the potential applications of nanotechnology in the construction industry and what the industry needs. Although certain sectors within the construction industry keep pace with the latest nanotechnology research breakthroughs, the industry as a whole does not lead the charge. The construction industry, which encompasses building and infrastructure construction, and environmental and petroleum engineering, could greatly benefit from a deeper understanding of the products and techniques enabled by nanotechnology. This could result in improved customer productivity and quality. This study gives careful consideration to the applications of nanotechnology in the field of construction.

Keywords: Nanomaterials, nanotechnology, nanoscience, construction, industry

INTRODUCTION

The word "nanotechnology" refers to the scientific and technological fields that utilize phenomena on the nanometer scale in the development, characterization, manufacturing, and application of materials, structures, devices, and systems. Although many natural structures, such as essential molecules within the human body and components of food, have nanometer dimensions (referred to as the nanoscale), and although many technologies have involved nanoscale structures for many years, it has only been possible to actively and purposely modify molecules and structures within this size range for the last quarter of a century.[1]

What sets nanotechnology apart from other technological fields is the ability to exert control at the nanometer scale. It is expected that people and businesses will benefit from the widespread use of nanotechnology, with many applications including novel materials that give dramatically different qualities through operating at the nanoscale where new phenomena occur due to the extremely high surface-to-volume ratios and quantum effects that do not exist at larger scales.[2,3] Industries that have quickly adopted nanotechnology include those dealing with information and communications, food technology, energy technology, and medical products.[1]

However, just as the nanoscale phenomena may offer benefits, they may also expose individuals and the environment to new health hazards, especially with the free nanoparticles created in nanotechnology processes.[4,5] Those working with free nanoparticles should be particularly concerned, as the novel properties of nanoparticles pose a potential threat to established defense mechanisms, including the immune and inflammatory systems.[6,7] The way that nanoparticles spread and persist in the environment also makes it possible that the end result of nanotechnology could harm the environment.[6,7]

WHAT IS THE STATE OF NANOTECHNOLOGY AND NANOSCIENCE TODAY?

The numerous fields that contribute to our current understanding of the nanometer scale are diverse, beginning with the molecules and atoms notions in chemistry and physics and expanding to include molecular life sciences, medicine, and engineering. Controlling and selectively modifying features of ever-smaller amounts of matter for practical purposes has been a natural progression from the study and comprehension of atomic and molecular behavior from basic principles. The early discoveries in self-assembly that led to modern synthetic and supra-molecular chemistry the growing understanding of life's replication processes, and the parallel development. As a result, disciplines like bimolecular and medical engineering, as well as the developing field of systems biology, are now a part of the modern molecular life sciences, which include topics like molecular motors and other functional entities.[8,9] On the other hand, micro- and nano-scale sensing devices made by humans come from other areas of microscopy and device engineering, but they can still be used in medicine.Surface effects, such

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Corresponding author:
Michael Toryila TIZA
E-mail: tizamichael@gmail.com

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as catalytic activity and wetting behavior in materials composed of nanosized entities like nanoparticles, composites, and colloids, sometimes have unexpected significance due to the deviation of surface and interface properties from the bulk properties of larger amounts of materials.[10,11] Clusters of very tiny particles, on the scale of a thousand atoms or molecules or fewer, exhibit surface features that are consistent with quantum mechanical principles. Materials with novel and optimized physical and/or chemical characteristics might be designed using composites.[12,13] Electronic engineering has advanced into the nanometer region, with gate oxides in devices typically being 25 nm thick. The self-assembly of structures resembling those of phospholipid bilayers, which mimic biological membranes, is a potential with the continued growth of nanotechnology, which might lead to the bottom-up manufacturing of nanoscale materials. However, the production of artificial biological systems by self-assembly and analogous processes, as proposed by several notable commentators, is deemed very implausible on the basis of existing understanding. The state of the art says that putting self-replication and self-perpetuation into engineered nanosystems is a very difficult task.[14,15]

CONCRETE TECHNOLOGY AND NANOTECHNOLOGY

Nanotechnology in concrete is among civil engineering's most common and fruitful applications. Over time, concrete changes into a more durable and attractive nanostructured multi-phase composite. There are bonded water molecules, crystals ranging in size from nanometers to micrometers, and an amorphous phase.[16] It is used for everything from constructing roads and bridges to erecting buildings. The addition of nanoparticles to concrete is just one of several possible alterations to the material. Nano-silica and nano-titanium oxide are the most often studied nanoparticles; however, nano-iron, nano-alumina, and nanoclay have also been the subject of considerable investigation.[17]

The construction industry devotes a disproportionate amount of R&D funding to concrete since it is the sole material used specifically for the building. In the following sections, we will take a look at some of the most exciting new uses of nanotechnology in construction that are either in the works or already on the market. Since much of the study describing concrete is undertaken at universities and research institutions, the information is freely available to the public. Several nanoscale scientific methods, such as atomic force microscopy (AFM), scanning electron microscopy (SEM), and focused ion beam (FIB), are being used to study the structure of concrete.[18,19-21]

The creation of these tools was spurred by a desire to learn more about the nanoscale in general, but applying that knowledge to better understand the underlying structure and behavior of concrete is a crucial and very relevant use of nanotechnology. There has already been research that crosses over the mechanical modeling of bones for medical engineering and that of concrete. This has allowed for the study of chloride diffusion in concrete, which shows one of the most important parts of nanotechnology: its ability to be used in many different fields. The next paragraphs detail how a better knowledge of concrete's nano-properties is opening up new possibilities for increasing its strength, durability, and monitoring. Regular concrete has silica (SiO_2) as an integral component. One of the advances made by nanoscale concrete research is the use of nano-silica to improve particle packing in concrete, which densifies the micro- and nano-structure and improves mechanical properties. The addition of nano-silica to cement-based materials has been shown to increase durability by preventing water penetration and slowing the deterioration of concrete's fundamental C–S–H (calcium–silicate–hydrate) reaction, which is a result of calcium leaching in water. High energy milling of regular Ordinary Portland Cement (OPC) clinker and normal sand reduces particle size more than traditional OPC, leading to a compressive strength that is 3-6 times higher than that of unrefined OPC.[22-24] The use of fly ash increases the durability and strength of concrete and, critically for sustainability, decreases the amount of cement needed; nevertheless, the curing of concrete is prolonged by the addition of fly ash, and early stage strength is low in contrast to conventional concrete. Fly-ash concrete's density and early on strength are enhanced by the inclusion of SiO_2 nanoparticles, which replace a portion of the cement. When hematite (Fe_2O_3) nanoparticles are incorporated into concrete, studies have shown that not only is the material stronger, but it also allows for stress levels to be monitored by the measurement of section electrical resistance.[25]

HYDROPHOBICITY IN CONCRETE

A substance is said to be hydrophilic and to exhibit hydrophilicity if it has the property of being attracted to water. On the other hand, a substance that is hydrophobic and exhibits hydrophobicity is one that drives water away. It is crazy to think about what has been mixed with concrete to try to figure out what happens by trial and error. For example, wastewater and hospital waste, glass, and even *E. coli* germs have all been used in this way. Although this is a part of the drive to produce ecologically efficient concrete, in terms of both energy and cement use, and to promote recycling, it is also related to the low-tech commoditized nature of construction materials, in that they are not designed from a scientific perspective but rather experimented with and adjusted empirically.[26,27] In point of fact, even some of the principles that are used in the design of structural concrete have been developed experimentally from behavior that has been observed. The study of nanotechnology, which entails the study of the fundamental components of concrete, has the potential to pave the way toward a genuine understanding of concrete construction and service life on the basis of a material that has been developed to have attributes that have already been identified. This has a close connection to the topic covered in the section on sustainability and the environment, which is the study of service life using multiscale modeling (encompassing several dimensional scales such as from nanometer to meter). Research has shown that the addition of an anaerobic (a microorganism that does not require oxygen) microorganism to the water used for mixing concrete results in a 25% increase in the material's strength after 28 days. This is just one example of the kinds of modifications that have been made to concrete. The Shewanella microbe was used at a concentration of 105 cells/mL, and nanoscale inspection demonstrated that there was a buildup of sand–cement matrix on the surface of the microorganism. Because of this, filler material began to form inside the pores of the cement–sand matrix, which resulted in the matrix being significantly more robust. This has major consequences for the longevity of concrete, and as a result, it contributes to sustainability by reducing the amount of material required. It is also a component of the larger area of "self-healing" materials, which also includes coatings, and its behavior is patterned, at least to some extent, on the behavior of naturally occurring "self-healing" or "self-assembling" processes.[26,27] In a similar fashion, the University of Illinois at Urbana–Champaign is working on developing autonomic (or spontaneous) self-healing polymers. These polymers make use of capsules that break open in order to fill fractures.[28,29]

CARBON NANOTUBE IN CONCRETE

Carbon nanotubes (CNTs) are a type of carbon atom that were found for the first time in 1952 in Russia and then rediscovered in the 1990s in Japan. Their name stems from the diameter of 1 nm, which gives them their characteristic cylinder form. They can be many millimeters in length and can have either a single "layer" or wall (referred to as a "single-walled nanotube" (SWNT)) or several layers or walls (multi-walled nanotube).[30,31] Nanotubes have a high cost of production, and their price per gram can range anywhere from €20 to €1000, depending on the quality. Because of their extraordinary qualities, CNTs are currently the subject of extensive study all around the world to determine their potential uses. For instance, they have Young's modulus that is 5 times higher and a strength that is 8 times higher (theoretically 100 times higher) than steel despite having just one-sixth of the density. Multi-walled tubes may glide telescopically without encountering any resistance, and depending on their precise construction, they can either be ballistically electrically conducting (without encountering any resistance) or semi-conductive.[32,33] Thermal conduction along the axis of the tube is likewise quite strong, although it is relatively low perpendicular to the axis. There is work being done to bring down the price of CNTs, and when that happens, the benefits that are given by adding CNTs to cementitious materials may become more appealing. For the time being, however, the cost of adding CNTs to concrete may be prohibitive.

TITANIUM OXIDE IN CONCRETE

Because of its bright white color, titanium dioxide (TiO_2) is often used as a white pigment. It can also oxidize oxygen or organic molecules, which is why it is used in paint, cement, windows, and tiles to provide sterilizing, deodorizing, and antifouling properties. When combined with outdoor construction materials, it can dramatically reduce airborne pollution concentrations. When exposed to ultraviolet (UV) light, TiO_2 can be utilized for anti-fogging coatings and self-cleaning windows because, when exposed to UV light, it becomes more hydrophilic (attractive to water). This characteristic enables its use in both of these applications. Titanium dioxide nanoparticles are another kind included in concrete to improve its properties. Titanium dioxide is a white pigment with excellent reflective qualities. It can function as a coating. Titanium dioxide is added to paints, cements, and windows for its sterilizing properties as a result of its powerful catalytic reactions that break down organic pollutants, volatile organic compounds, and bacterial membranes. It is also utilized as a UV-blocking nanoparticle in sunscreen. When sprayed on outdoor surfaces, it can cut down on the number of pollutants in the air.[34-36]

In addition, due to its hydrophilic nature, it provides self-cleaning properties to any surface onto which it is applied. This occurs when precipitation is pulled to the surface and condenses into sheets. These sheets then collect and remove the contaminants and dirt particles that were previously broken down. In contrast to the stained buildings of the material's pioneering history, the resulting concrete has a white hue that retains its whiteness exceptionally well. This concrete has already been utilized in global construction projects. Carbon nanotubes are an extra type of nanoparticle with outstanding properties (box 3, page 8).

Current research is examining the advantages of adding CNTs to concrete, and this research will continue in the near future. The mechanical properties of samples largely composed of water and the principal Portland cement phase can be improved by the addition of CNTs at concentrations as low as 1% by weight. Oxidized multi-walled nanotubes (MWNTs) exhibit the greatest increases in compressive strength (+25 N/mm^2) and flexural strength (+8 N/mm^2) in comparison to the reference samples without reinforcement. This is true for both compressive and flexural strength. It is believed that the higher defect concentration on the surface of the oxidized MWNTs contributes to a better interaction between the nanostructures and the binder, hence improving the composite's mechanical properties. This is comparable to the deformations of reinforcing bars.[37,38] The addition of CNTs to any material, however, leads to the tubes clumping together and a lack of cohesion between them and the bulk material matrix. These are 2 possible disadvantages of the technique. As a result of the interaction between the graphene sheets that make up nanotubes, the tubes have a tendency to cluster together to form bundles or "ropes," and these ropes can even become twisted. In order to achieve a uniform distribution, it is necessary to disentangle them. In addition, due to their graphitic nature, there is imperfect adhesion between the nanotube and the matrix in nature, resulting in sliding. This is a consequence of their interaction. However, the mechanical properties can be enhanced when the nanotubes are pre-dispersed with gum Arabic. This is particularly true for SWNTs. More study is required to establish the optimal proportions of carbon nanotubes and dispersion agents that should be included in the mix design parameters.[39]

APPLICATIONS OF NANOTECHNOLOGY IN COATINGS

Significant nanotechnology research is being conducted on coatings, including those for concrete, glass, and steel (all of which are discussed above). Many processes, including chemical vapor deposition (CVD), dip coating, meniscus coating, spray coating, and plasma coating, are used to deposit a layer onto a substrate and bond it to the base material, giving the surface the necessary durability and functionality. The main goal of testing and modeling coatings is to give them the ability to heal themselves through a process called "self-assembly." Paints with nanotechno logy-enhanced insulating qualities are already on the market.[39] These features result from the inclusion of nano-sized cells, holes, and particles, which significantly reduce heat conduction (R values are twice as high as those of insulating foam). This type of paint is used to keep metal from rusting because it repels water. It can do this by stopping water from coming out of a metal pipe and protecting the metal from salt water.[40-42]

In addition to the possibilities for concrete discussed in the section on "Nanotechnology and Concrete," there may be uses for stone-based materials. Although resins are often used to reinforce these materials and prevent fracture, the aesthetics and adherence to substrates might suffer as a result of these resin treatments. Nanoparticle-based systems have the potential to outperform more traditional methods in terms of adhesion and transparency. In addition to the self-cleaning coatings for windows discussed above, TiO_2 (box 2, p. 7) nanoparticles are also being tested as a coating material for use on highways all over the world due to their exceptional qualities. Coating 7000 m^2 of road in Milan with TiO_2 resulted in a 60% reduction in nitrous oxides, which indicates that the coating is effective in capturing and decomposing both organic and inorganic air pollutants through a photocatalytic process. The potential environmental benefits of putting roads to good use are explored in this study.[43]

STEEL AND NANOTECHNOLOGY

Steel has played a significant role in the building industry since the second industrial revolution in the late 19th and early 20th centuries. The European Union produces a total of 185 million metric tons of steel per year, and because of its widespread usage in industries such as automotives that are located close to the building sector, the industry receives a sizable share of research money. In the following paragraphs, we will look at how nanotechnology is already being put to use in the steel industry, as well as some of the most promising places where it may go in the future.[44]

Steel in structures that experience cyclic loads, like bridges or towers, is vulnerable to fatigue, which can cause structural failure. This can happen at stresses much lower than the yield stress of the material, greatly reducing the usable life of the structure. Current design tenets need a shorter permitted service life, a shorter allowable stress range, or a more frequent inspection schedule. This is a sustainability and safety concern due to the fact that it greatly increases the expense of building maintenance over the course of a building's lifetime and reduces the efficiency with which resources may be used. Copper nanoparticles added to steel reduce surface unevenness, limiting the amount of stress risers and, as a result, fatigue cracking, according to researchers. Safety would improve, monitoring would be unnecessary, and resources could be used more effectively in building projects where fatigue is a problem. Stronger cables may now be made thanks to recent developments in refining the cementite phase of steel to nano-size. Because high-strength steel cables are used not only in car tires but also in bridge construction and in precast concrete tensioning, a more durable cable material would shorten the time and money needed to build a bridge, especially a suspension bridge, because the cables are strung from end to end.[45,46]

In addition to improving sustainability, increasing cable strength also improves efficiency. Strong bolts are necessary for the high-strength joints used in tall buildings. To achieve their strength, high-strength bolts are often quenched and tempered to create their tempered martensite microstructure. Small amounts of hydrogen brittle the grain boundaries of tempered martensite steel with tensile strengths above 1200 MPa, potentially leading to material failure in service. Delay in the fracture is a problem that has prevented steel bolts from being made any stronger than about 1200 MPa. Nanoparticle research on vanadium and molybdenum has revealed that they alleviate the delayed fracture issues common to high-strength bolts. The nanoparticles improved the steel microstructure by dampening the impact of the inter-granular cementite phase, and the reduction of hydrogen embrittlement was a contributing factor. When subjected to unexpected dynamic loads, welds and the heat-affected zone (HAZ) close to welds can become brittle and fail without notice, making weld toughness a major concern, especially in seismically active regions. After the Northridge earthquake in the Los Angeles area in 1994, a reevaluation of welded structural joints was conducted in light of the resulting weld and HAZ failures. Modern design philosophies include the deliberate oversizing of structures to keep all stresses low or the selective weakening of structures to produce controlled deformation away from brittle welded joints.[46] However, recent studies have demonstrated that increasing the HAZ grain size (to roughly one-fifth the size of normal material) in plate steel using nanoparticles of magnesium and calcium can boost weld toughness. An improvement in toughness at welded joints would decrease the resource need since less material would be needed to keep stresses within permitted limits. This is a sustainability problem as well as a safety one. Despite carbon nanotubes' promising properties of strength and stiffness, they have found little use as an addition to steel because their inherent slipperiness (due to their graphitic nature) makes them difficult to bind to the bulk material and they pull out easily, rendering them ineffective. Another obstacle to CNTs' efficient usage as a composite component is the high temperatures used in steel production and their impact on the material.[47]

THE IMPACT OF NANOTECHNOLOGY ON THE CONSTRUCTION INDUSTRY

The building industry is significantly influenced by nanotechnology. Several applications have been developed specifically for this sector of the economy to improve the durability and functionality of building materials; the effectiveness of energy-saving measures; the safety of structures; the ease with which maintenance can be performed; and the level of comfort experienced by residents. Despite the fact that self-cleaning properties can be achieved with micron-sized coatings and surface treatments such as TeflonTM, polysilazane-based coatings, etc., these properties have become a marketing tool or slogan for nanotechnology applications, especially in consumer markets like construction, textiles, etc. A nanoparticle coating made of TiO_2, Al_2O_3, or ZnO is what gives building ceramics their anti-slip qualities. With the aid of UV light, TiO_2 may, with the aid of TiO_2, break down dirt and pollutants on surfaces such as tiles, glass, and sanitary ware, making it easier to remove them with rain. Coatings and paints containing ZnO are more resistant to the destructive effects of UV light. Nanosized Al_2O_3 particles are responsible for the material's scratch resistance. Additionally, these ingredients hinder the formation of mold, mildew, and other organisms that generate musty and disagreeable odors. Nanotechnology will improve the performance of cement, concrete, and steel, the 3 most commonly used construction materials. When nanoparticles are added to concrete, the material becomes more robust, damage-resistant, self-healing, air-purifying, fire-resistant, easily cleanable, quickly compactable, and able to withstand high temperatures. Nanosilica (also referred to as silica fume), nanostructured metals, CNTs, and carbon nanofibers (CNFs) are only some of the nanoparticles that have the potential to be employed for these purposes.[48-50] Research on the use of nanotechnology to improve cement manufacturing conditions and reduce CO_2 emissions is being driven in part by the current push to reduce cement production's CO_2 emissions. This study seeks to enhance cement manufacturing conditions and minimize CO_2 emissions. Using nanotechnology-based coatings, graffiti, and other unpleasant markings may be prevented on concrete.In addition, it is anticipated that nanotechnology will aid in the manufacture of novel, durable, flame-resistant, self-healing, and lightweight building materials, such as revolutionary nanocomposites. The implementation of nanotechnology will result in significant modifications to glass and, by extension, windows. The term "smart windows" is a marketing term for windows with several functions, such as UV protection, energy efficiency, and cleanliness. Photovoltaics is another of these capabilities. Nanotechnology has opened the door to the prospect of enhanced insulating characteristics and smart buildings that might increase energy efficiency. The development of nanotechnology has enabled the manufacture of new insulating materials. For example, nanofoams, nanostructured aerogels, and vacuum-insulated panels (VIPs), among other things, are used as insulation today. In the future, embedded sensor technology will make it feasible to construct smart homes. These technologies will enable buildings to detect their surroundings and respond appropriately.[51] In theory, the construction industry has unlimited potential for utilizing nanoparticles and enjoying the benefits of nanotechnology. However, one of the most important questions that must be addressed is how well these technologies will perform in the market.[52]

Construction mainly depends on cement and, eventually, concrete. The characteristics of these materials determine the structural strength, durability, quality, and sustainable expansion of buildings, bridges, and other structures. Concrete has been used as a building material since the Stone Age. The main component of concrete is cement. To make cement, calcium carbonate (limestone) and other ingredients, such as silicon, aluminum, and iron oxides, are crushed and ground into a fine powder. In order to do this, a kiln is required to fire the mixed material to extremely high temperatures (1400-1500°C), forcing the compounds to react. Clinker refers to the nodules that the final items emerge from the kiln. Cement is made by grinding together cooled clinker with smaller amounts of gypsum, fly ash, aggregates, and other ingredients.[53,54]

Cement is combined with sand, gravel, and water to produce concrete, which is subsequently used for construction. Changes to concrete can be made to make it stronger, more flexible, better at insulating against heat and sound, and have other good qualities. Because the material is made from natural sources with flaws, its size can range from nanometers to centimeters. By adding reinforcements such as steel bars, glass fiber, etc., the strength of concrete is increased. Each year, almost 2 billion metric tons of cement are manufactured worldwide. Europe contributes to 25% of the production of this industry. This equates to approximately 1.7 m^3 of concrete per person per year, or approximately 750 million m^3 of concrete. About 4 out of the 5 biggest cement companies in the world are based in Europe. China annually consumes 1.2 billion tons of cement, making it the largest consumer in the world.[55,56]

NANOTECHNOLOGY'S IMPACT ON CEMENT CONCRETE

If the cement industry is to stay competitive, it must adopt cutting-edge technology and invest substantial resources in R&D to assure the continuous development of these time-tested building blocks. Understanding how cementitious materials behave on the nanoscale and microscale is a big part of cement research, which aims to improve cement's mechanical properties and length of use. Reducing CO_2 emissions throughout the lifetime of concrete, which begins with the production of cement, is also vital. This is why a number of large cement makers are investing in research aimed at simultaneously reducing CO_2 emissions and enhancing the material's performance. Interactions at the nanoscale or microscale have a big effect on the mechanical properties of concrete in the end, so it is important to understand and describe its basic structure and how it forms.[57]

Nanotechnology's unique characterization approaches are especially valuable in this instance since they enable us to better appreciate the mechanism of action underneath the surface of the concrete building we're analyzing. The density of the porosity impacts the durability of the concrete. In other words, rheology requires management. This is possible with the aid of current mathematical and modeling advancements. The durability of concrete is influenced by ultrafine particles. Therefore, enhanced control structures would increase the strength and durability of concrete. Controlling the behavior of cement hydrates at the nanoscale might provide insight into their unusual tendencies. Nanotechnology has also changed the concrete industry by making it possible to use nanoparticles, such as nanosilicates, to speed up the rate at which concrete hardens.[58]

Quick-setting or self-compacting concrete is becoming more popular in the construction industry because it can be used in projects where the concrete needs to be strong quickly, like within 4 hours in airport building projects, etc. Ingredients, structure, and heat treatments all contribute to this capability. Utilizing nanosilicates might help you get the required strength in less time. Nanoadditives make concrete last longer by making it stronger mechanically. This is good news for the cost of maintaining and fixing older buildings. One of the most polluting industries, the making of concrete and cement, is responsible for 5% of all CO_2 emissions in the world. When limestone is converted to clinker for the production of cement, approximately 0.8 tons of carbon dioxide are emitted into the atmosphere. Because of this, any invention that could reduce emissions would help the economy and progress a lot. Cement makers want to use nanoparticles to either replace clinker with other ingredients (like fly ash, limestone, pozzolan, etc.) or use less clinker. Reducing carbon dioxide emissions is a top priority for the cement industry, and nanotechnology may provide solutions.[59] Cement businesses are presently concentrating on lowering kiln temperatures through the use of nano additives and repurposing construction materials. Limestone is constantly put through a chemical process called calcination, or decarbonation, which releases CO_2 into the air. Also, because fossil fuels are used in the basic thermal process, it gives off more CO_2.[60]

Cement companies have come up with a number of ways to deal with this problem, such as using nanoparticles as a supplementary cementing agent in cement production. This could replace clinker and lower the clinker ratio. By using nanoparticles as a catalyst to speed up the reaction and lower the Gibbs free energy, the amount of clinker that is needed can be minimized or made as good as it can be. This would allow reactions to occur at lower temperatures, thereby lowering the demand for fossil fuels. When nano TiO_2 particles are added to concrete, it gets the same easy-to-clean photocatalytic qualities as ceramic tiles and sanitary items. In the case of its application to concrete, in addition to offering a self-cleaning function, it also contributes to the cleaning of surfaces, notably highways, of nitrogen oxide particles generated by exhaust fumes. This is done by a surface process called photocatalysis, which turns dangerous nitrogen oxide (NOx) into harmless nitrate (NO_3).[61] It has been shown that using nanotechnology-enhanced concrete on roads lowers the amount of NOx that comes out of car exhaust. For this effect, microscopic TiO_2 particles are required on concrete roadways. When UV light and nanoparticles of TiO_2 are present, photocatalysis occurs, which aids in the collection and decomposition of organic and inorganic air contaminants. This concrete anti-graffiti coating is also self-cleaning. Concrete science research has also been done on how to stop concrete from breaking or help it heal, for example by controlling the release of corrosion inhibitors.[62]

CONCLUSION

Civil engineering may get significant benefits from nanotechnology. Because of this, several problems with building with concrete and steel have been fixed, and the quality of these materials has been improved. Nanotechnology has also helped people come up with better and more durable materials, like concrete and glass, that clean and fix themselves. Nanotechnology-based coatings may be utilized to improve a wide range of qualities, including fire resistance, corrosion resistance, insulation, among others. Nanotechnology has the potential to enhance the quality and availability of water. Future civil engineers, like me, will need to know about nanotechnology, so this is the most important thing for me to learn about. It is simple to understand why nanotechnology is so vital to civil engineering and why it should be introduced into the engineering curriculum. Nanotechnology is important to the progress of civil engineering, but it won't make a big difference in the field until it's taught to a wider audience and all those who want to become civil engineers.

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Carbon Footprint Evaluation of a Ready-Mixed Concrete Plant

Mahmut YEŞİLYURT
Beyhan KOCADAĞISTAN

Department of Environmental Engineering, Atatürk University, Faculty of Engineering, Erzurum, Türkiye

ABSTRACT

Rapid population growth and the vital needs of people are increasing day by day. One of these needs is nutrition, clothing, and shelter. As the housing needs of people increase, the construction and building sector is progressing in parallel with technological developments. Innovations related to the production of ready-mixed concrete and cement, which are indispensable building elements of the construction sector, make human life easier. These sectors should be evaluated in terms of greenhouse gas emissions and sustainable environment. Identifying, calculating, and reporting data in these sectors for carbon footprint calculation contribute to environmental issues and development for consumers and organizations. In this study, the carbon footprint of a ready-mixed concrete plant is calculated, and its environmental impacts and suggestions for reducing carbon emissions are given. It was found that the total carbon emission caused by consumption amounts was 1 038 396 tons of carbon dioxide equivalent. According to the results obtained in the carbon footprint in the greenhouse gas calculation, 98.383% of the total emission (1 021 604 tons of carbon dioxide equivalent) is carbon dioxide emission, 0.149% (1551 tons of carbon dioxide equivalent) is methane emission, and 1.468% (15 242 tons of carbon dioxide equivalent) is diazot monoxide emission.

Keywords: Cement, ready-mixed concrete plant, carbon footprint, life cycle

INTRODUCTION

With the advancement of age, climate changes and population growth are increasing day by day and bringing along many environmental problems. In this sense, the most important environmental problems are resource scarcity, increasing amounts of greenhouse gases (GHGs), rising temperature, climate changes, natural disasters, and disruption of ecological balance.[1,2] The consumption of fossil fuels with the industrial revolution has led to a rapid increase in GHG emissions in the atmosphere, with carbon dioxide (CO_2) levels reaching dangerous levels.[1,3,4] Global warming and environmental pollution are caused by production, manufacturing, all kinds of industrial activities, agriculture, transportation, construction, the construction sector, mining, energy production and use, and human activities.[1,4] Today, the construction sector ranks first among the sectors monitored to meet the needs of the growing population and the needs it brings with it in order to achieve a sustainable beneficial economy, and at the same time, it ranks second after transportation in terms of the total GHG emissions it generates.[5,6] When carbon emissions and resource use in the construction sector are evaluated together, energy consumption, especially during the production of building materials, accounts for 20% of the amount consumed during the production of buildings and construction structures. This is very significant in terms of GHGs.[7-9] Such emissions are also caused by the carbon content of additives, auxiliaries, and building materials used in the construction industry, and it has been emphasized that recycling and switching to environmentally friendly additives will reduce these emissions.[9,10] Concrete, ready-mixed concrete, and cement, which have a large share in the construction sector, are materials with a high global carbon footprint due to their high carbon content and are the most widely used building materials in this field.[10,11] As environmental awareness increases, the materials used in the construction sector play an important role in the choice of environmentally sensitive materials, and while these materials are diversified in parallel with the development of technology due to energy and material costs, recycling methods are applied (6%) and the use of alternative additives is becoming widespread.[12,13] Properties such as durability, applicability, and versatility play an important role in the selection of materials used in the construction industry. On the other hand, low CO_2 emissions is a new parameter that plays a role in the selection of materials used, and new methods to reduce them have been investigated in recent years.[14]

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Corresponding Author:
Mahmut YEŞILYURT
E-mail: umyesilyurt@gmail.com

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READY-MIXED CONCRETE AND CEMENT INDUSTRY

As a requirement of rapid population growth, industrialization and urban life, modern urban structures, buildings, roads, bridges, infrastructure systems, water and wastewater systems are made of concrete, ready mixed concrete and cement-based concrete.[12,15] Cement and concrete are preferred as construction and building materials due to their durability, ease, and wide range of availability. According to the 2019 data, the amount of carbon emissions from power, energy, and fossil fuels used in these production processes and in the transfer transportation phase is considerable and accounts for approximately 10% of global emissions. It is environmentally important to take measures to reduce these impacts. These measures include turning to alternative building materials and auxiliary elements, producing environmentally friendly materials, developing technologies to minimize environmental risks, promoting recycling, and developing building materials for a sustainable environment.[12]

The production of concrete, which is widely used in the construction sector with global growth and population increase, is over 3.8 tons per person per year in the world; concrete has an important value in carbon footprint assessment due to its high CO_2 emissions during the manufacturing and supply process. For this reason, its environmental impacts are taken into account and controlled in developed countries, especially in European countries.[16,17] In 2021, the number of companies in the sector increased by 11% and the number of facilities increased by 7% in Türkiye compared to the previous year. While the number of ready-mixed concrete companies in Türkiye was 25 and the number of facilities was 30 in 1988, these values increased to 450 and 900 in 2019. And with an increase, the number of ready-mixed concrete companies reached 600 and the number of facilities reached 1106 in 2022.[18] Table 1 shows the amount of ready-mixed concrete production in the world and Türkiye. Policies and action plans should be developed on a global scale to reduce the production of concrete, ready-mixed concrete, and cement to meet the needs of the age.

In the modern era, CO_2 emissions from the production and shipment of cement, the most widely used building material and a critical component of both concrete and mortar, account for approximately 2.4% of global emissions. In the process of clinker production in limestone quarries or other raw carbonate mineral sources, which are the main building blocks of cement production, calcium carbonate ($CaCO_3$) is calcined into quicklime (CaO), the main component of cement, during which the largest carbon emission occurs as a result of the combustion of fossil fuels.[15,19] More than 4 billion tons of Portland cement are produced in the world annually, depending on the demand.[20-24] In developing countries like Türkiye, this need is increasing day by day, leading to an increase in the accumulation of GHGs.

Table 1. Ready-Mixed Concrete Production in the World and in Türkiye

	2020	2021	2021	2021	2021
Austria	11.5	12.8	255	50.2	1.4
Belgium	12.4	14.0	235	59.6	1.2
Denmark	2.8	3.1	96	32.3	0.5
Finland	2.9	2.9	193	15	0.5
France	37.0	40.6	1856	21.9	0.6
Germany	55.3	54.2	1900	28.5	0.7
Ireland	4.7	4.7	220	21.4	0.9
Italy	28.7	35.8	1800	19.9	0.6
Netherlands	7.4	7.2	188	38.3	0.4
Poland	25.7	26.6	1096	24.3	0.7
Portugal	5.7	6.2	231	26.8	0.6
Slovakia	3.0	2.9	280	10.4	0.5
Spain	22.8	25.8	1601	16.1	0.5
England	20.7	23.6	1062	22.2	0.4
Israel	20.8	21.1	226	93.4	2.4
Norway	3.7	3.6	208	17.3	0.7
Türkiye	95.0	105.0	1106	94.9	1.3

Carbon Footprint

Carbon dioxide constitutes a large proportion of GHGs released into the atmosphere. Since it has the largest proportion among GHGs, it is accepted and used as the main component in the "carbon footprint" calculation. The concept of carbon footprint was first introduced in the 1990s by William E. Rees and Mathis Wackernagel, sustainable environmental advocates, as part of the ecological footprint concept.[25] Carbon footprint calculation is the calculation of CO_2, methane (CH_4), nitrous oxide, and fluorinated gases released into the atmosphere as a result of vital activities under the name of GHGs (in equivalent amounts). The carbon footprint value of that individual or community is defined for the carbon dioxide (CO_2) emissions thrown into the nature as a result of the vital activities of individuals or societies.[26] Greenhouse gas sources, which come to the fore with the transition to modern life and population growth, are emissions from energy production, vehicle use and public transportation, industrial and agricultural uses, and other similar activities. The carbon footprint basically consists of 2 main parts. These are called primary and secondary carbon footprints. The main component of the primary carbon footprint is CO_2 emissions resulting directly from the use of fossil fuels for domestic and industrial heating and lighting, energy consumption for power, and transportation. Secondary carbon footprint is expressed as indirect CO_2 emissions resulting from the production, use and degradation of all products in nature. According to the Intergovernmental Panel on Climate Change (IPCC), 3 main approaches are used to calculate the carbon footprint with this data. These approaches, called tiers, consist of 3 different categories. These are the 1st tier, 2nd tier and 3rd tier approaches.

In the tier 1 approach, the calculation is made using data from national energy statistics and the amount of fuel and emission factors according to the type of fuel used. In the tier 2 approach, in addition to tier 1, specific emission factors and combustion technologies for the country or specific regions are used. In the tier 3 approach, fuel statistics and technology-dependent emission factors determined according to the combustion technology and the thermal power of the combustion plants and statistical information are used.[27] Figure 1 shows the GHG sources and their boundaries. Since the amount of CO_2 is high in this model, general calculations are made in terms of equivalent CO_2 (Equation 1), while the total amount of carbon is calculated from Equation 2.[21,28]

$$CO_2eq[kg] = CO_2[kg] + 25 \times CH_4 + 298 \times N_2O \tag{1}$$

$$Total\ Carbon\,(GgC) = ET\ (TJ) \times CEF\left(\frac{tC}{TJ}\right)10^{-3} \tag{2}$$

where ET represents energy consumption (TJ) and CEF represents carbon emission factor (tons of carbon/TJ).[28]

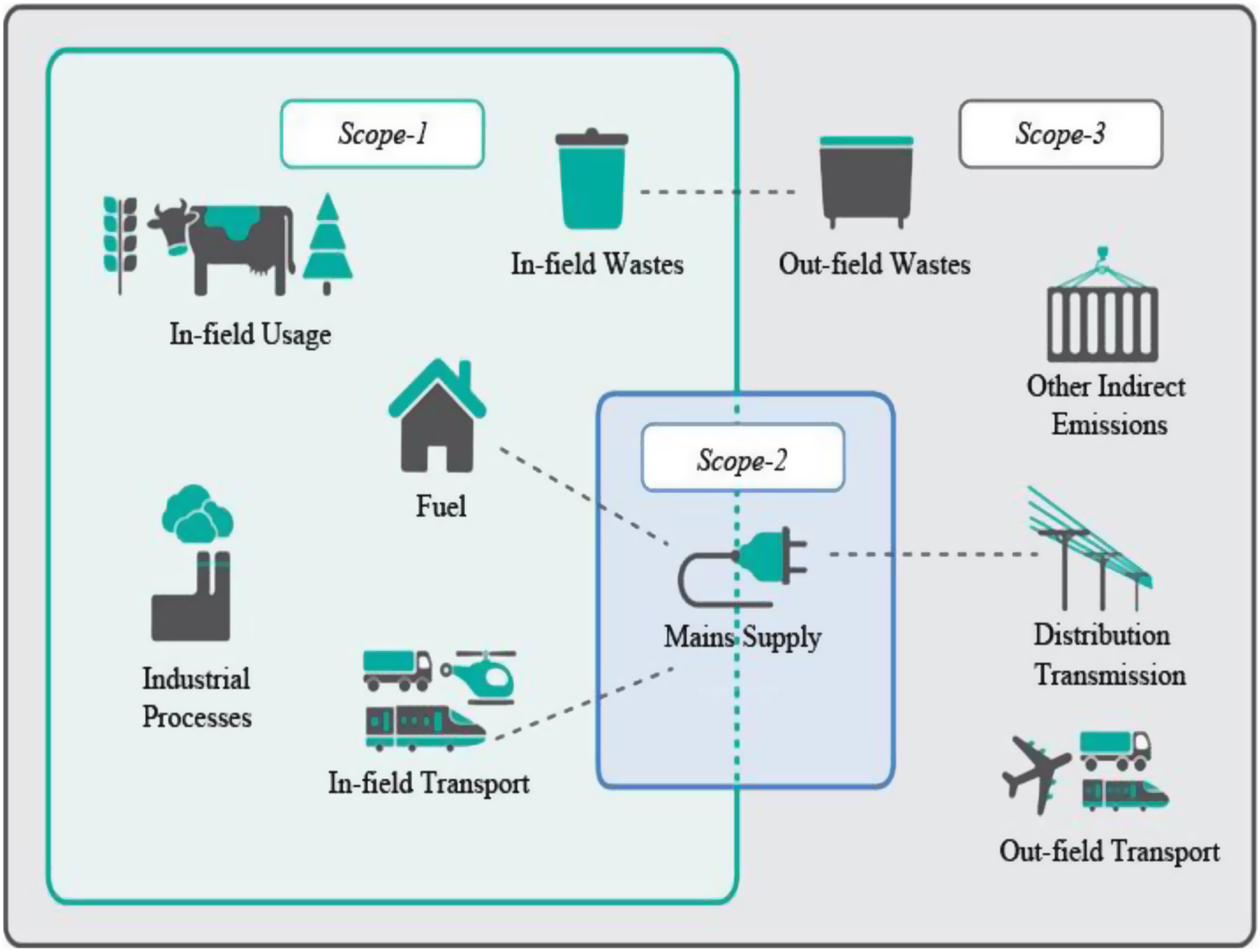

Figure 1. Greenhouse gas sources and their limits.[27]

According to the IPCC, the concept of global warming potential (GWP) has been developed to compare the impact of anthropogenic GHGs on the atmosphere. Specifically, GWP is a measure of how much energy it would take to emit 1 ton of a gas over a given period of time compared to the emission of 1 ton of CO_2. According to the GWP magnitude, the potential to increase the atmospheric temperature is calculated.[29] Carbon dioxide equivalent is used to assess and quantify different gas emissions based on GWP values. It is obtained by multiplying the $kgCO_2$ equivalent in kilograms by the corresponding GWP. That is, $kgCO_{2e}$ = (the weight of the gas in kg) × (the GWP value of the gas.[30]

In 2020, a 10% reduction in GHG emissions in the USA was observed (according to United States Environmental Protection Agency data) with the regulations made since 2019, especially with the use of 11% less fossil fuels, the transition to less carbon-intensive natural gas and renewable resources, and the use of electrical energy.[31] The data on the distribution of carbon emissions by sectors in the USA are given as 27% for transportation, 25% for electricity generation, 24% for industry, 11% for livestock, 7% for trade, and 6% for households. The resulting GHGs are 3% fluorogases, 7% nitrogen oxides, 11% CH_4, and 79% CO_2.[31]

Cement Industry Greenhouse Gas Emissions

The energy used during cement production accounts for 12%-15% of the total energy used in industries.[32] Dry cement production steps consist of raw material production, kiln preparation, baking clinker calcination, and cement grinding and packaging. Carbon dioxide emissions from cement production are mainly composed of 3 main components:

1. Carbon dioxide emissions from the degradation of limestone containing calcium carbonate ($CaCO_3$) and $MgCO_3$ during clinker production: here, process-related CO_2 emissions are directly caused by the degradation of raw materials.
2. Carbon dioxide emissions related to the fuel used during the process: here, high temperature is required for clinker calcination. Fossil fuels (coal, petroleum coke, and natural gas) and alternative fuels (plastic, rubber, and sludge) can be used in cement production.
3. Electricity-related CO_2 emissions: these emissions are indirectly caused by electricity consumption.[33]

Typical GHG rates from the cement sector are given in Table 2.[34]

Since a significant amount of GHG carbon emissions in the cement sector occurs during clinker production, the tier 3 method is used in production-based calculations. The process is based on input

Table 2. Cement Industry Greenhouse Gases

Component	Concentration
CO_2	14%-33% (w/w)
NO_2	5%-10% (w/w)
NO_x	<200-3000 mg/Nm^3
SO_2	<10-3500 mg/Nm^3
O_2	8%-14% (v/v)

methods based on raw materials and the volume and chemical composition of clinker and dust from the kiln system.[33,35] The distribution of carbon emissions by sectors in the USA is given as 27% for transportation, 25% for electricity generation, and 24% for industry, production, raw materials and binders. While natural substances increase the cost of using raw materials, a decrease in emissions has been observed.[13,36] Of the total GHG components, about one-third of CO_2 emissions are reported to come from the industrial sectors, emitting 2370 TJ of CO_2, which is 43% of the total. Depending on the type of fuel used, it is estimated that about 0.9-1.0 tons of CO_2 is emitted per ton of clinker and 0.65-0.92 tons of CO_2 is emitted from 1 ton of cement production.[32,37,38]

Ready-Mixed Concrete Plant Greenhouse Gas Emissions

The elements that affect GHG in ready-mixed concrete production are cement, aggregate, water, chemical, and auxiliary additives, and the component that causes the highest emission is cement. For the production of 1 ton of clinker, approximately 0.9-1 ton of CO_2 emission occurs. Emissions also occur during the transportation of aggregates and binders. As the transportation distance increases, vehicle fuel consumption and exhaust emissions also increase.[39] Greenhouse gases generated in the production of ready-mixed concrete are produced during the preparation and transportation of compositions such as limestone, gravel and sand, aggregate and water for use.[40] Emissions can be reduced by reducing the energy and resource use during the preparation and transportation of the product, which is concrete that has not yet hardened and has not been transported to the construction site using a mixer.[41] Since CO_2 emissions in ready-mixed concrete plants are calculated in terms of energy consumption per unit of material produced, examples of reducing the carbon footprint of concrete and concrete structures depend on the use of raw materials. For example, emissions during the production of Portland cement were found to be higher than the use of ecofriendly other materials.[42] In this sense, ground-granulated blast furnace slag, a by-product of the steel industry, causes minimum carbon emissions when used as fly ash additive. In addition, when environmentally friendly recycled materials are selected for concrete use and when reduction in water use is emphasized with innovative approaches, emission amounts are also reduced.[43,44] The production and use of ready-mixed concrete in the construction industry and the steel and cement used as building materials consume approximately 40% of all energy and 1% of transportation and shipping costs.[2,30] Preventing the pollution of natural resources and new approaches to energy use are important components that reduce the carbon footprint.

Carbon Footprint Management

Framework setting, data collection, collaboration with stakeholders, statistical evaluations, calculations and reporting are essential in carbon footprint management. Calculations are based on the consumption amount according to the sectors and the carbon emission factor according to the relevant IPCC calculation data. Various improvements to reduce the carbon footprint have become mandatory for both a sustainable economy and a sustainable environment. When determining the carbon footprint, enterprises should determine the assessment of risks and measures to be taken in the light of statistical data to determine environmental impacts. Regular controls should be carried out in all business units, processes should be monitored, staff should be trained, all expenses of the enterprises should be audited, and energy reduction measures should be investigated.[45,46] The environmental problems arising from ready-mixed concrete plants were evaluated by classifying them as the amount and types of energy used, solid waste management, air, water, soil pollution emission amounts and types, and fossil fuels used. By evaluating and reducing these impacts, environmental risks will also be reduced.[47] Technological developments play an important role in the calculation and reduction of carbon emissions for a sustainable environment in the production and transportation of concrete and cement. Material quality in cement and concrete production with the zero carbon principle, design and features for architects and engineers, use and post-use disposal and recycling processes are a whole evaluated as.[22] Sanctions and regulations should be managed by governments to control sustainable practices. The use of alternative cement and concrete products should be encouraged by following developments and innovations, and practices such as accelerated carbon capture should be implemented to ensure long-term sustainability. A significant amount of waste is generated in ready-mixed concrete plants every year. In the management of these wastes, crushing and screening the hardened concrete returned to the plant and recycling it for use as aggregates would be a positive environmental approach. In 1 study, it was found that concrete with recycled aggregates in Brazil has economically favorable conditions.[48]

By using recycled concrete, resource reduction and indirect emission reduction can be achieved. The part of concrete waste that can be recycled consists of 70% aggregate. The remaining 30% is non-recyclable paste (a combination of cementitious materials, water, partially hydrated cement, or pozzolanic reacted products). A system can be installed that can recover quality aggregates by washing the cement paste with fresh or gray water generated during washing.

In addition, gray water from aggregate reclamation, dust suppression, or other cleaning processes, such as washing the inner surfaces of mixer drums and mixer truck wheels, can be used for beneficial environmental management. Carbon and water footprints can be reduced through environmental approaches, many of which are based on energy and resource recovery. It is important to take the necessary measures for a sustainable environment. Since energy is the most important parameter in concrete plants, the use of waste heat as an alternative energy source, implementation of innovative CO_2 capture and storage technologies, sequestration of CO_2 by increasing biological absorption capacity in forests and soils, and the use of blended cement by reducing the clinker/cement ratio should be expanded. Other important measures include increasing the use of renewable energy sources or nuclear energy and the use of alternative raw materials including fly ash, slag, gypsum, anhydrite, and fluorite using non-carbonated calcium raw materials.[32,34,49] The production and environmental impacts of ready-mixed concrete used in housing and infrastructure works in urban areas in Latin America and the Caribbean were examined, and it was determined that 7.16 tons of material was used for the production of 2 604 862 m^3 of ready-mixed concrete, of which 99.1% were primary raw materials and 0.9% were secondary raw materials. It was observed that 5.36 tons (~78.6%) of the material used here was aggregate and the emission value was ~19.5% of the total Equivalent CO_2 eq. It was found that by using recycled aggregates instead of Portland cement used in this process, a saving of 20% in the use of raw materials can be achieved to ensure sustainability in building materials.[21]

MATERIALS AND METHODS

The ready-mixed concrete batching plant, whose carbon footprint is calculated, has a total area of 17 855 square meter, 953 square meter closed. There are 33 employees in the facility, and the number of workers may increase seasonally depending on the increase in workload. A total of 116 000 m^3 of ready-mixed concrete was produced at the facility in 2021. For this production, raw materials were transported, electricity and water were consumed, coal was used in the facility for heating purposes, and the concrete produced was delivered to the buyer in transmixers. The activities that cause carbon footprint formation as a result of the ready-mixed concrete production activity can be counted as transportation, electricity consumption, water consumption, and facility heating. All vehicles in the facility use diesel fuel, and coal is used as the fuel for heating purposes. All data used in this study are taken from the company's records. Consumption data for 2021 are given in Table 3, the site plan of the ready-mixed concrete plant is given in Figure 2, and the flowchart is given in Figure 3.

According to the workflow of the plant, ready aggregate is discharged into the bunker with the help of construction machinery, and this material is conveyed to the washing and screening point

Table 3. Consumption of Concrete Plant Data

Consumption Data	Quantity (Per Year)
Diesel fuel (L)	329 629
Solid fuel (lignite coal) (kg)	10 000
Water (L)	22 791 200
Electricity (kW)	703 112.92

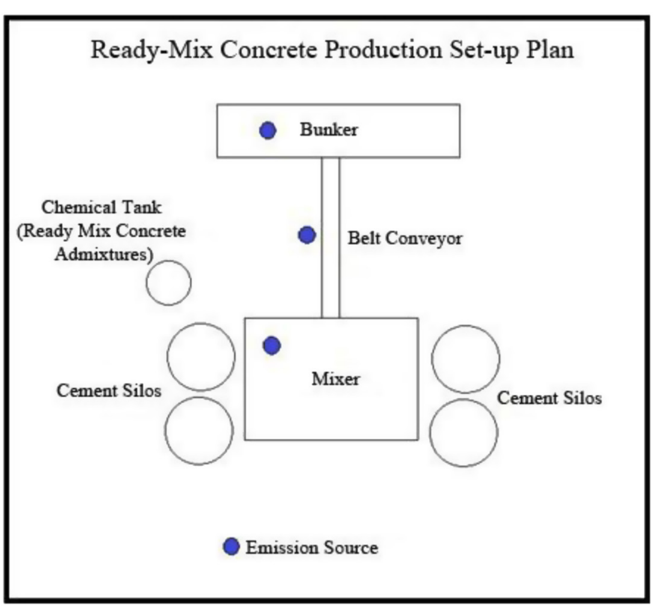

Figure 2. Ready-mixed concrete production site plan.

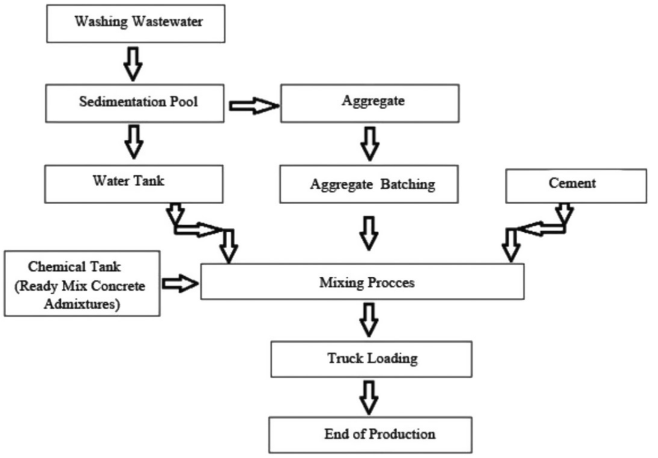

Figure 3. Ready-mixed concrete production work flowchart.

with the help of conveyor belts and from there to the stockyard. Meanwhile, the washed sand prepared in the plant is also discharged into the bunker with the help of construction machinery. In addition, with the help of moving belts, the material in the bunker is conveyed to the mixing boiler with the help of the water pump in the water tank and the cement augers in the cement silos. All materials coming to the mixing boiler are mixed in the desired proportions in this boiler. The ready-mixed concrete produced is filled into mixer vehicles from the filling point. Mixer vehicles returning to the plant at the end of the working day are washed with water in the inclined area in the first step of the settling pool. The wastewater coming out of this pool is transferred to the second pool with the help of a pipe, and the water waiting here is allowed to settle. The water remaining on the surface is taken to the next pool and sent to the water tank with the help of a pump. All of the wastewater generated as a result of washing the mixers is reused within the system, preventing waste generation.

RESULTS AND DISCUSSION

Based on the consumption data of the ready-mixed concrete plant, calculations were made using the tier 1 method formulas specified in the IPCC report. While making the calculations, the calorific values of the emission factors given separately for each record in the IPCC report were taken as the basis. Emission factors determined by Department for Food, Environment and Rural Affairs (DEFRA) were used in the carbon footprint calculation for electricity consumption and water consumption. While calculating the carbon footprint for fossil fuels, the GWPs of CH_4 and diazot monoxide (N_2O) emissions resulting from the combustion process are calculated by converting them into CO_2 equivalent, which has the largest proportion among GHGs. The carbon emission amounts obtained as a result of the calculations are given in Table 4.

According to the calculation results, it was found that the total CO_2 equivalent emission caused by consumption amounts was 1 038 396 tons of CO_{2e}. Of this total emission, 98.383% (1 021 604 tons CO_{2e}) is CO_2 emission, 0.149% (1551 tons CO_{2e}) is CH_4 emission, and 1.468% (15 242 tons CO_{2e}) is N_2O emission (Figure 4).

How the total amount of emissions is proportioned to the consumption data is also shown graphically in Figure 5. When the total CO_2 equivalent emission is evaluated according to the

Table 4. Ready-Mixed Concrete Plant Greenhouse Gas Emissions

Emissions	Quantities (tCO_{2e})
CO_2 emission	
Diesel	871.746
Lignite	12.019
Electricity	134.442
Water	3.396
CH_4 emission	
Diesel	0.964
Lignite	0.025
Electricity	0.562
Water	0.000
N_2O emission	
Diesel	14.223
Lignite	0.055
Electricity	0.963
Water	0000
Total	1038.396

consumption sources of the ready-mixed concrete batching plant, it can be seen that diesel fuel consumption (886 933 tons CO_{2e}) has the highest emission rate of 85.414% and water consumption (3396 tons CO_{2e}) has the lowest emission rate of 0.327%.

How the consumption ratios for specific gases are calculated is also shown graphically in Figures 6-8.

When all calculations are analyzed, CO_2 and N_2O were found to be the gases with the highest and lowest emission rates, respectively, while diesel fuels were found to have the highest

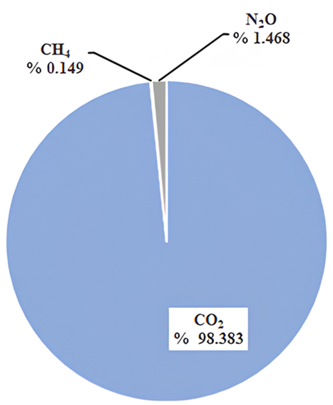

Figure 4. Distribution of total CO_2 equivalent emissions by gases. CH_4, methane; CO_2, carbon dioxide; N_2O, diazot monoxide.

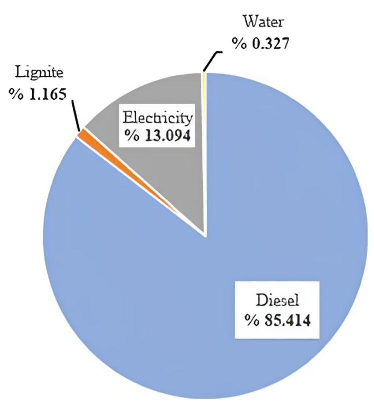

Figure 5. Distribution of total carbon dioxide equivalent emissions by sources consumed.

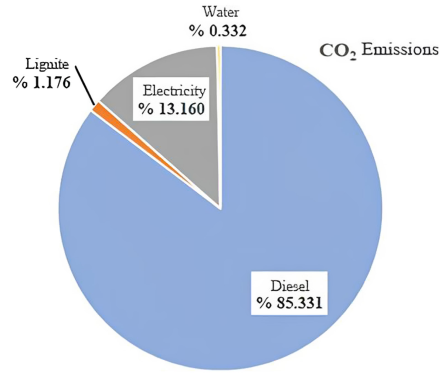

Figure 6. Distribution of carbon dioxide (CO_2) emissions according to the resources consumed.

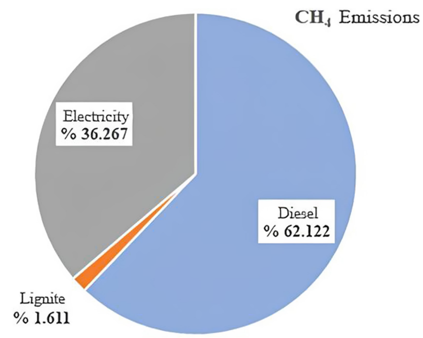

Figure 7. Distribution of methane (CH_4) emissions by sources consumed.

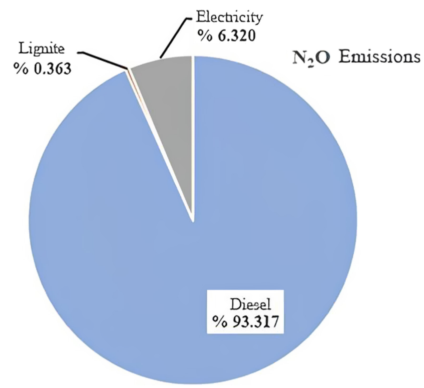

Figure 8. Distribution of diazot monoxide (N_2O) emissions according to the resources consumed.

contribution to carbon emissions when evaluated on the basis of consumed resources.

CONCLUSIONS

The production of concrete, ready-mixed concrete, and cement, which are the main components of housing and infrastructure, roads, water and wastewater systems, and all kinds of buildings and structures, emit a significant proportion of GHGs emitted worldwide. Sustainable construction and sustainable economy should be targeted for carbon reduction through innovative technology and advancements in the ready-mixed concrete sector. In order to reduce the carbon footprint, energy efficiency should be increased, waste heat recovery should be maximized, waste should be utilized, and alternative raw materials should be used by reducing the use of Portland cement. Governments should also introduce new regulations and standards for cement-based materials. Innovative solutions in the use of cement-based concrete and zero carbon understanding should be supported on behalf of humanity.

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Platinum/Vulcan XC-72R Electrocatalyst Doped with Melamine for Polymer Electrolyte Membrane Fuel Cells

Pınar ÇELİK
Ayşe BAYRAKÇEKEN YURTCAN

Atatürk University, Engineering Faculty, Chemical Engineering, Erzurum, Türkiye

ABSTRACT

Polymer electrolyte membrane fuel cells are the common type of fuel cells for stationary and portable applications. The main purpose of fuel cell research and development studies is to develop low-cost, high-performance, and durable materials. For this purpose, higher performance is targeted by reducing the cost of polymer electrolyte membrane fuel cell electrocatalysts. The use of carbon black in polymer electrolyte membrane fuel cells has been quite high in recent years. In this study, first platinum on carbon black electrocatalyst was synthesized via microwave irradiation method and then melamine as nitrogen source at a mass ratio of (1:1) for melamine:electrocatalyst was prepared. Examining the physicochemical and electrochemical characterizations of the electrocatalyst is very important for understanding their performance, durability, and material properties. Therefore, the synthesized electrocatalyst was characterized by using elemental analysis, inductively coupled plasma mass spectrometry and transmission electron microscope analysis. In addition, the fuel cell performance of the electrocatalyst was tested in a single fuel cell test hardware.

Keywords: PEMFC, electrocatalyst, nanoparticles, nitrogen doping, melamine

INTRODUCTION

Fuel cells are systems that convert chemical energy directly into electricity.[1] Fuel cells are divided into different groups according to the type of reactants used, electrolyte type, and operating temperatures.[2,3] Among the various fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) stand out with their features such as high power density,[4] low operating temperatures (60-80°C),[5] high reliability,[2] fast start-up times,[5,6] and zero/low emissions.[7] However, despite all these advantages, the main disadvantage of PEM fuel cells is their cost. In recent years, scientists have carried out different studies in order to commercialize PEM fuel cell technology and increase its performance.

The PEM fuel cells are composed of PEMs to provide proton conductivity and electrocatalysts for half-cell reactions.[8] One of the reasons for using platinum-based electrocatalysts in PEM fuel cells is their oxygen reduction reaction (ORR) activities and their relatively high stability in the acidic and oxidizing environment of the PEMFC cathode.[9] Due to the high cost of platinum (Pt), several studies were carried out in order to decrease the amount of Pt.[10] The electrocatalyst preparation method affects the pore size, surface area, morphology and physical properties of the synthesized electrocatalysts whereas the structure and composition of the support material and active catalytic component affects the chemical properties.[11] Commonly used carbon supports provide new active sites to increase the catalytic activity.[12] Pre-treatment of carbon materials can significantly increase their catalytic activity for ORR and change their electrochemical behavior.[13-15] One of these pre-treatments is the doping of carbon materials with heteroatoms such as nitrogen. Nitrogen doping on carbon support materials can be performed using the pyrolysis method.[16] In recent years, nitrogen-doped carbon materials have been widely used as support materials in fuel cell electrocatalysts for the homogeneous distribution of Pt nanoparticles. It was also suggested that nitrogen doping provides improvements for ORR in Pt/carbon (C)-based fuel cell electrocatalysts.[17] Nitrogen doping with melamine has positive effects on the performance of supercapacitors and energy storage devices.[18,19]

In the literature, mostly nitrogen doping is applied to the electrocatalyst support materials. In this study, our goal is to reduce the amount of platinum electrocatalyst and increase the performance of the fuel cell by doping the electrocatalyst other than the support material. First, the carbon black support material (Vulcan XC-72R, VXR) was decorated with Pt nanoparticles by microwave irradiation method and Pt/VXR electrocatalyst was obtained. Pt/VXR was mechanically mixed with melamine due to its high nitrogen content of 66.7%[20,21] at a mass ratio of 1:1 and after pyrolysis, the (Pt/VXR) + melamine-(1:1) electrocatalyst was obtained for PEMFC.

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Corresponding author:
Ayşe BAYRAKÇEKEN YURTCAN
E-mail: abayrakceken@atauni.edu.tr

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EXPERIMENTAL

Synthesis of Nitrogen-Doped Electrocatalyst

In the synthesis of nitrogen-doped electrocatalyst, first Pt nanoparticles were deposited on carbon black (Vulcan XC-72R, VXR) support material by microwave irradiation method. The nominal amount of Pt targeted on the support material is 20%. After the Pt reduction process on the support material, it was washed and then dried for 12 hours at 100°C. After drying, Pt/VXR electrocatalyst and melamine were mixed mechanically with a mass ratio of 1:1 and then pyrolyzed for 2 hours at 900°C in a nitrogen gas environment. The synthesized electrocatalyst was used at the cathode side and commercial Pt/C electrocatalyst (Tanaka, 67%) was used at the anode side. The anode, cathode, and the membrane were hot pressed to prepare the membrane electrode assembly (MEA).

Characterizations

It is expected that the electrocatalysts prepared for use in the PEM fuel cell will have features such as high activity, high selectivity, and stability. It is very important to understand the physicochemical and electrochemical characterizations of the structures of the electrocatalysts in order to achieve these properties. In this study, the structures of the synthesized electrocatalysts were investigated using physicochemical and electrochemical characterization techniques.

The LECO CHNS 628 model Elemental Analyzer was used to quantitatively determine the amount of nitrogen in the synthesized electrocatalyst. Inductively coupled plasma-mass spectrometry (ICP-MS) Agilent 7800 device was used to determine the amount of Pt over the support material, while Hitachi HighTech HT7700 device was used for transmission electron microscope (TEM) analysis. Finally, the prepared electrocatalyst was turned into MEA and its performance was tested under atmospheric pressure in a fuel cell station (HenatechTM, 600 W).

RESULTS AND DISCUSSION

Elemental Analysis Result

The nitrogen amount of the electrocatalyst was analyzed by using elemental analysis. Element analysis data are given in Table 1. According to this process, the nitrogen amount of (Pt/VXR) + melamine-(1:1) electrocatalyst is obtained as 2.67%. From the results obtained, it is seen that the nitrogen doping process with the pyrolysis method is successful. The nitrogen amount change will significantly affect the activity of the electrocatalyst.[22]

Inductively Coupled Plasma-Mass Spectrometer Analysis Result

Inductively coupled plasma-mass spectrometer analysis was performed to obtain information about the Pt loading amount in the synthesized Pt/VXR + melamine-(1:1) electrocatalyst. The targeted nominal amount of Pt on the support material in the prepared electrocatalyst is 20%. The ICP-MS result is given in Table 2. According to this table, the loaded Pt (% by mass) amounts were obtained as 13.9% which was lower than the nominal value.

Transmission Electron Microscope Result

The Pt nanoparticle distribution over carbon support material and particle size of Pt nanoparticles in the synthesized electrocatalyst were analyzed by TEM analysis. The TEM image of the electrocatalyst at 50 nm and the particle size histogram plot are given in Figure 1. Particle sizes were calculated from TEM images by using the ImageJ program. It was seen that the sizes of Pt nanoparticles loaded on the carbon support have an average of 7 nm.

Polymer Electrolyte Membrane Fuel Cell Test Results

(Pt/VXR) + melamine-(1:1) electrocatalyst was tested in a PEM fuel cell test station using a single fuel cell hardware. The polarization curve for the corresponding electrocatalyst is given in Figure 2. It is more appropriate to evaluate the performance of

Table 1. Elemental Analysis Result

	Elements, %			
Electrocatalyst	C (%)	H (%)	N (%)	S (%)
(Pt/VXR) + melamine-(1:1)	78.46	1.2	2.67	0.43

Pt/VXR, platinum/Vulcan XC-72R.

Table 2. ICP-MS Result

Electrocatalyst	Pyrolysis Temperature (°C)	Pt (% by Weight)
(Pt/VXR) + melamine (1:1)	900	13.9

ICP-MS, inductively coupled plasma-mass spectrometry; Pt/VXR, platinum/Vulcan XC-72R.

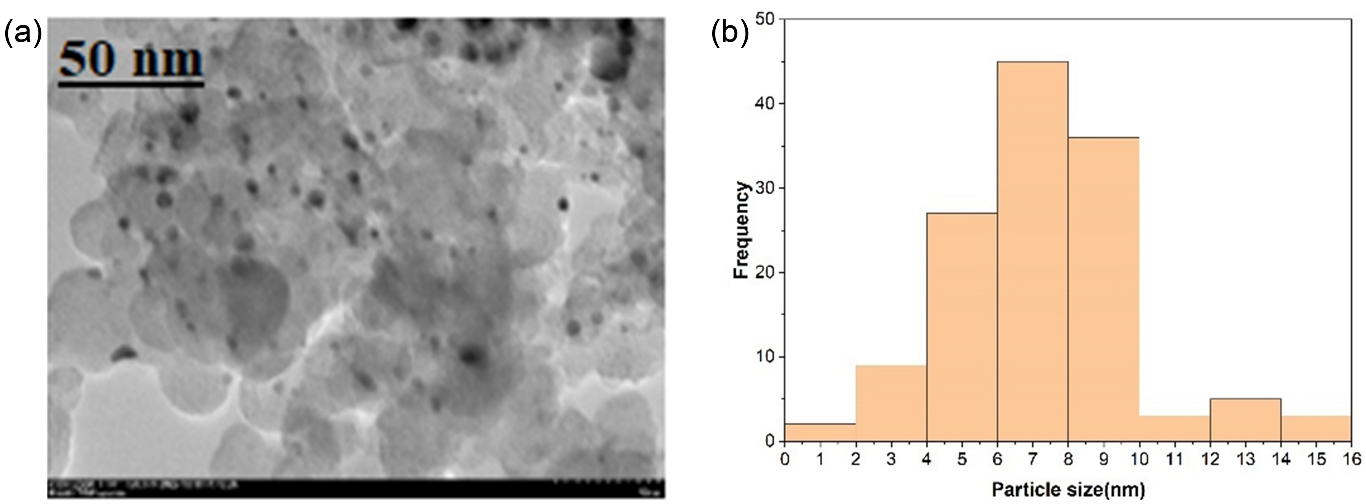

Figure 1. (Pt/VXR) + melamine-(1:1) electrocatalyst (A) TEM image at 50 nm; (B) particle size histogram. Pt/VXR, platinum/Vulcan XC-72R; TEM, transmission electron microscope.

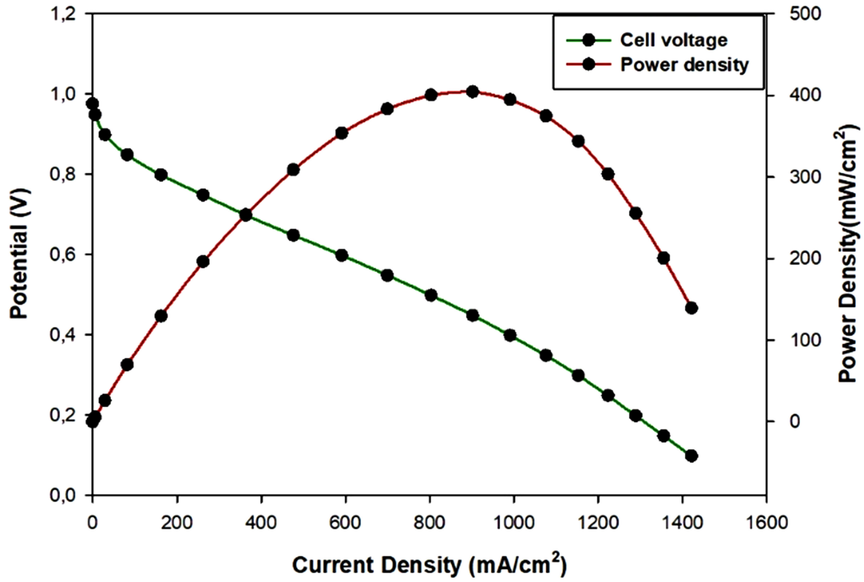

Figure 2. PEM fuel cell polarization curve. PEM, polymer electrolyte membrane.

Table 3. Current and Power Density Values at 0.6 V for (Pt/VXR) + Melamine-(1:1) Electrocatalyst

	@ 0.6 V	
Electrocatalyst	*i* (mA/cm2)	*P* (W/cm2)
Pt/VXR + melamine-(1:1)	591.3	353.6
Pt/VXR	513.2	306.9

Pt/VXR, platinum/Vulcan XC-72R.

the electrocatalyst layer at 0.6 V, as it generally strikes a balance between fuel cell efficiency and practical power output.[23] For this reason, the current and power density values corresponding to the PEM fuel cell performance of the electrocatalyst prepared using Pt/VXR and melamine at a mass ratio of 0.6 V (1:1) and the Pt/VXR values prepared without adding melamine in order to make comparisons are summarized in Table 3. According to the graph in Figure 2, the measured values of (Pt/VXR) + melamine-(1:1) electrocatalyst at 0.6 V were obtained as 591.3 mA/cm^2 current density and 353.6 mW/cm^2 power density which was higher than the melamine-free electrocatalyst.

CONCLUSIONS

According to the elemental analysis results, nitrogen doping with the pyrolysis process was successful, but the Pt loading on the support material was lower than the nominal value. In TEM analysis, it was observed that Pt nanoparticles showed a homogeneous distribution on the electrocatalyst surface. The PEM fuel cell performance test shows a current density of 591.3 mA/cm^2 and a power density of 353.6 mW/cm^2 for the (Pt/VXR) + melamine-(1:1) electrocatalyst based on values measured at 0.6 V. The melamine-free Pt/VXR catalyst synthesized under the same conditions (with the same Pt loading rate and pretreatment) showed a current density of 513.2 mA/cm^2 and a power density of 306.9 mW/cm^2, according to the values measured at 0.6 V. (Pt/VXR) + melamine-(1:1) catalyst showed better fuel cell performance than melamine-free Pt/VXR catalyst. According to the results obtained from the fuel cell performances, it can be said that nitrogen doping of the electrocatalyst seems to be a promising way.

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NanoEra

Research Article

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Excitation-Dependent and pH-Sensitive Fluorescence Emission of Carbon Quantum Dots from Whey as Precursor

Ahmet Burak İLTER[1]
Selin AYDIN[2]
Aslı YILMAZ[2]
Mehmet YILMAZ[1,3]

[1]Atatürk University, Department of Nanoscience and Nanoengineering, Erzurum, Türkiye
[2]Atatürk University, Department of Molecular Biology and Genetics, Erzurum, Türkiye
[3]Atatürk University, Department of Chemical Engineering, Erzurum, Türkiye

ABSTRACT

Fluorescent carbon nanoparticles or carbon quantum dots, a novel type of nanomaterials, have been introduced with their unique chemical, optical, and biological properties. Due to their high biocompatibility and non-toxicity, low cost, and unique emission properties, carbon quantum dots have become the focus of attention in nanotechnology in a short time. Thanks to these features, they provide opportunities for use in many fields such as biotechnology, bioimaging, drug release, biosensors, photocatalysis, and, solar cells. In addition to these advantages, they may offer excitation wavelength-dependent properties and the pH-sensitive photoluminescence mechanism. In this study, we present a simple yet environmentally friendly method to produce carbon quantum dots from whey, an important dairy waste. For this, carbon quantum dots were synthesized by hydrothermal synthesis using whey as the precursor for 24 hours at 220°C. The fabricated carbon quantum dots exhibited a bluish-white emission under ultraviolet light with an excitation-dependent property. Also, as the pH value increased, the fluorescence activity decreased accordingly without any remarkable shift in absorption maxima indicating the potential application of carbon quantum dots as pH sensors in various chemical and biological systems.

Keywords: Carbon quantum dots, excitation-dependent emission, whey, hydrothermal synthesis, pH sensor

INTRODUCTION

Carbon quantum dots (CQDs) are novel carbon-based nanomaterials that have been proposed in the last two decades as an alternative to their conventional counterparts such as inorganic semiconductors and fluorescent dyes.[1,2] Typically, CQDs are in the range of 2-15 nm with a carbon-based skeleton and various functional groups on the surface.[3–6] Many parameters including chemical content, nanoparticle size, and distribution as well as the type of surface groups intensively govern the physical, chemical, and resultant optical nature of CQDs.[7–9] With their unique structures, CQDs offer advantages in terms of high fluorescence activity with photostability, low cytotoxicity, high biocompatibility, high solubility, flexible surface structures, easy functionalization of the surface structure, chemical stability, and low cost.[4–6,10,11] Thanks to these unique properties, CQDs are widely employed in many fields such as chemical sensing, bioimaging, photocatalytic applications, and nanomedicine.[12–20]

To date, significant progress has been performed regarding the production and applications of carbon quantum dots. Both top-down and bottom-up approaches have been utilized for the production of CQDs. In the case of the top-down approach, the size of carbon-based raw material is reduced to the nanoscale after the application of chemical or mechanical processes including electrochemical oxidation, laser ablation, arc discharge, and high-energy ball milling.[21–25] These techniques require high energy and expensive and complicated devices and lead to poor control over the size and content of the fabricated CQDs which are the major drawbacks of the approach that must be considered. In the bottom-up approach, atomic or molecular structures are used to fabricate materials on the nanoscale. In this context, various strategies including microwave-assisted, chemical vapor deposition, combustion, ultrasonic-assisted, solvothermal, and hydrothermal methods have been widely utilized for the fabrication of CQDs.[26,27] However, the hydrothermal method is the most preferred method due to its low cost, simplicity, and high reproducibility.[26,27] In the hydrothermal method, the processes are carried out in an aqueous solution in a closed system at a relatively high temperature (>100°C) and pressure (>1 atm). In general, the optical and chemical structure of resultant CQDs can be manipulated by the main process parameters such as synthesis temperature and time, initial pH, and the type of precursor.

So far, various organic materials including urea, lactic acid, and dopamine have been employed in the fabrication of CQDs via hydrothermal synthesis.[4–6] This approach dictates the usage of the precursors

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Corresponding author:
Mehmet YILMAZ
E-mail: nano.yilmaz@gmail.com

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with high costs. Recently, the employment of biomass waste from various sources such as agriculture and livestock, organic domestic waste, forestry, and related industries has been proposed as precursors of CQDs.[28–30] These sources provide significant advantages in terms of low-cost, renewable, and, environmentally friendly material with easy access. Also, this approach eliminates the treatment of industrial waste.

Herein, we propose the usage of whey as industrial waste from the dairy plant in the fabrication of CQDs via hydrothermal synthesis. We detected that the resultant CQDs exhibited high photoluminescence (PL) activity with pH-sensitive fluorescence nature in a wide pH range (4-9) indicating their potential applications in monitoring pH in various chemical and biomedical systems.

MATERIALS AND METHODS

For the synthesis of CQDs, whey was obtained from a local dairy plant in Erzurum as the precursor. Then, the whey was passed through filter paper (ISOLAB, 125 mm) to eliminate the suspending impurities. The appropriate amount of the whey was mixed with 10 mL of distilled water. The mixture was transferred to a Teflon-coated stainless steel reactor (40 mL) and kept in the oven for 24 hours at 220°C. At the end of the period, the reactor was cooled to room temperature and centrifuged at 13,000 rpm for 1 hour to remove aggregate structures.

An Agilent Cary Eclipse fluorescence spectroscopy (Santa Clara, Calif, USA) was used to determine the fluorescence nature of the prepared CQDs. Absorption spectra were collected by using ultraviolet-visible (UV-vis) spectroscopy (Shimadzu, UV-1800, Kyoto, Japan). The size and morphology of the particles were characterized using transmission electron microscopy (TEM, Hitachi Hightech HT7700, Tokyo, Japan). The pH of the CQDs was measured via a Mettler Toledo pH meter (Columbus, Ohio, USA).

RESULTS AND DISCUSSIONS

In this study, we basically aimed to determine the fluorescence nature and potential applications of CQDs obtained from whey, an important dairy waste product. For this, we employed the hydrothermal synthesis approach at 220°C for 24 hours. After the purification step, we collected fluorescence spectra at different excitation wavelengths and UV-vis absorption spectra (Figure 1). It was observed that the increase in excitation wavelengths in the range of 280-600 nm led to an obvious red shift in the fluorescence maxima from 478 to 622 nm (Figure 1A). This phenomena obviously indicate the excitation-dependent nature of the resultant CQDs. Also, the optical image of nano-colloid suspension exhibited a pale yellow color in daylight due to the carbonization of substances in whey (see inset in Figure 1A). Also, under a UV lamp (365 nm), the CQDs emitted a strong and bright bluish-white emission (see inset in Figure 1A). In UV-vis absorption spectra (Figure 1B), a weak peak maximum was observed at 291 nm indicating π-π^* transition. This transition can be attributed to the presence of aromatic C-C bonds in the structure of CQDs.[4–6] It seems that the whey as a precursor used for this synthesis was sufficiently carbonized to produce CQDs with high and excitation-dependent fluorescent activity.

After evaluating the optical properties, we collected some TEM images to analyze the morphology and size distribution of CQDs (Figure 2). From TEM images, we detected irregularly shaped carbon nanomaterials with amorphous structures (Figure 2A). The particle size distribution analysis showed that the size ranged

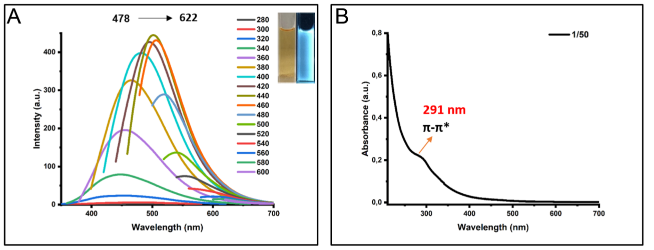

Figure 1. Fluorescence spectra of carbon quantum dots at different excitation wavelengths (A) (inset, optic images under daylight (left) and a 365-nm UV light (right)) and UV-vis absorption spectra (B). UV, ultraviolet; vis, visible.

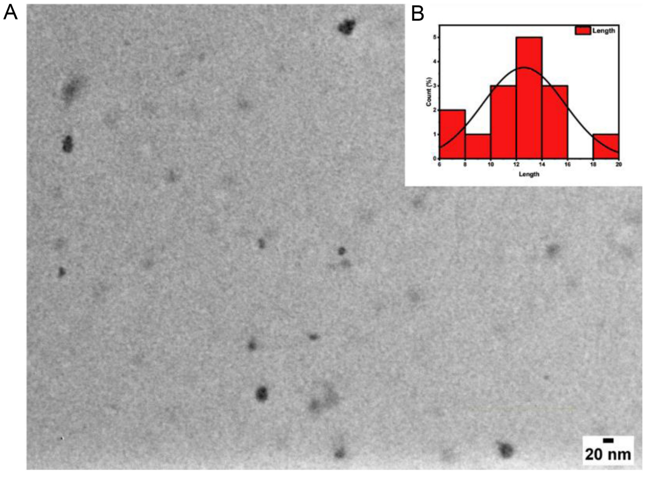

Figure 2. TEM image (A) and histogram plot (B) of CQDs showing particle size distribution. CQDs, carbon quantum dots; TEM, transmission electron microscopy.

from 8 to 20 nm with an average of 13.3 nm. The wide size distribution of CQDs may create a wide fluorescence emission for almost all visible ranges and resultant bright bluish-white emission. This issue must be furtherly investigated which will be the topic of our next study.

Finally, we checked the PL activity of CQDs over a wide pH range (4-9). We collected fluorescence spectra and their normalized intensity at different pH values (Figure 3). The maximum PL activity was observed for a pH value of 4. As the pH increases, the PL intensity decreases accordingly without any remarkable shift in absorption maxima. Considering the pH range of living organisms, we may conclude that the proposed CQDs can be employed as pH sensors for a given pH range. In our next study, this application of these nanosystems will be tested to determine pH-based imaging of living cells.

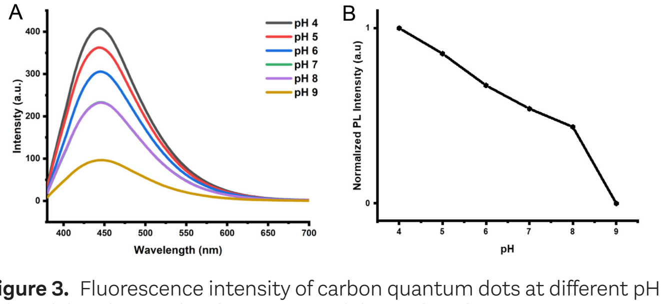

Figure 3. Fluorescence intensity of carbon quantum dots at different pH values (A) and normalized PL intensity (B). PL, photoluminescence.

CONCLUSIONS

In this study, we fabricated CQDs with excitation-dependent nature via a simple and low-cost hydrothermal method using whey as industrial waste from the dairy plant. With the increase in excitation wavelengths, an obvious red shift in the fluorescence maxima from 478 to 622 nm was observed probably due to the wide size distribution of CQDs with a wide fluorescence emission for almost all visible ranges and resultant bright bluish-white emission. As the pH of the CQD suspension increased, the PL activity decreased accordingly without any remarkable shift in absorption maxima. We envision that the proposed CQDs may be employed as pH sensors to monitor pH in various chemical and biomedical systems.

Peer-review: Externally peer-reviewed.

Author Contributions: Concept – M.Y., A.Y.; Design – A.B.I., S.A., M.Y.; Supervision – M.Y., A.Y.; Resources – M.Y., A.Y.; Materials – M.Y., A.Y.; Data Collection and/or Processing – A.B.I., S.A., M.Y.; Analysis and/or Interpretation – A.B.I., S.A., M.Y.; Literature Search – A.B.I., S.A., M.Y.; Writing Manuscript – M.Y., A.Y.; Critical Review – M.Y., A.Y.

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Research Article

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Enzymatic Bio-mining of Balkaya Lignite Coal with Bovine Carbonic Anhydrase Enzyme

Azize ALAYLI[1]
Yaşar DEMİR[2]
Nazan DEMİR[2]

[1]Sakarya University of Applied Sciences, Faculty of Health Science, Sakarya, Türkiye
[2]Muğla Sıtkı Koçman University, Department of Science, Department of Chemistry, Muğla, Türkiye

ABSTRACT

Carbonic anhydrase is a metalloenzyme containing zinc in its active center. In this study, the use of carbonic anhydrase enzyme in the bio-mining of Balkaya lignite coal has been matched. Carbonic anhydrase (carbonate hydrolyses: E.C. 4.2.1.1) was purified from bovine erythrocytes using a Sepharose-4B L-tyrosine sulfanilamide affinity chromatography. Hydratase and esterase activity of the enzyme were determined. The purity of the enzyme was recognized by single band on a sodium dodecyl sulfate-polyacrylamide gel electrophoresis. Then, Balkaya lignite coal with the size −20 mesh was investigated to break into pieces by using purified enzyme carbonic anhydrase with affinity chromatography. As a result of the bio-mining experiments, the carbonic anhydrase enzyme grounded Balkaya lignite coal. It was understood that the purified enzyme made smaller 1.75-fold of the Balkaya lignite coal within 96 hours using a shaker against the blank. When using a magnetic stirrer in the experiments were shown the enzyme made a smaller 73.75-fold against the blank. The results of these experiments showed that the enzyme carbonic anhydrase can be successfully used in the bio-mining of lignite coal of the same type.

Keywords: Bovine, carbonic anhydrase, Balkaya lignite, coal, bio-mining

INTRODUCTION

Carbonic anhydrase (CA) was first isolated from mammalian red blood cells. It is a zinc-containing metalloenzyme.[1-4] It catalyses in the below reaction (Figure 1).

Carbonic anhydrases are produced in a variety of tissues where they participate in a broad range of physiological processes such as acid–base homeostasis, carbon dioxide and ion transport, respiration, bone resorption, renal acidification, gluconeogenesis, ureagenesis, and the formation of cerebrospinal fluid and gastric acid.[5] The expanding a-CA gene family includes 11 enzymatically active members with different structural and catalytic properties. The cellular distribution and physiological functions of the various CA isozymes have been extensively described in several recent reviews.[6-8]

Preparation of the solid-liquid suspensions of coal carrying, storage, and handling facilities has very great practical importance. Coal-liquid dispersion stability of suspensions of solid particles has been dispersed, or aggregation environment against the resistance of the suspension depends on the size.

In the aggregation of solids such as coal, the grain size of the barrier due to mechanical operations, could not be bellowed by a certain limit. For this, a number of additional procedures were needed, such as wet grinding and chemical breakup. In particular, the chemical breakup has disadvantages such as high pressure and the need for inert gas. The geometries of the lignite particles change during the mechanical process. In addition, high pressure and mechanical friction on the surface of coal due to high temperature caused oxidation.

In this study, it was investigated whether the CA enzyme could be used in the bio-mining of Balkaya lignite coal.

EXPERIMENTAL

Bio-mining Materials

Lignite coal abundantly obtained from the Erzurum-Balkaya excavation area ground with a cell-mill to sizes of 20 mesh as to ASTM.

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Corresponding Author:
Nazan DEMİR
E-mail: nazdemir@mu.edu.tr

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$$H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

Figure 1. The reaction catalysis with carbonic anhydrase.

Purification of Bovine Carbonic Anhydrase

For obtaining the bovine CA enzyme, blood samples taken from Erzurum slaughterhouse were centrifuged (2500 rpm, 15 minutes, 4°C). The plasma was removed carefully. The precipitates were washed with saline 3 times. Then 40-50 mL of red cell pack was obtained from 100 mL of whole blood by this procedure. The resultant red cell pack was mixed with chilled distilled water at a ratio of 1/15 and left for 30 minutes until the completion of hemolysis. To isolate the membrane structure, the hemolysate was centrifuged (20 000 rpm, 30 minutes, 4°C). The supernatant was taken and its pH was adjusted to 8.7 with solid Tris, and then it was then applied to the affinity column.[9]

Affinity Chromatography

An affinity column was used for the separation of CA, which has a matrix composed of Sepharose-4B activated by CNBr and having covalently bound L-tyrosine arms. In the last step of the column preparation, the diazotized sulfanilamide was attached to the L-tyrosine arms. One hundred milliliters of hemolysate mentioned above was applied to the column. Then it was washed with 400 mL of 25 mM Tris–HCl/22 mM Na_2SO_4 (pH 8.7), giving rise to CA attachment and removal of undesirables. By adding 0.1 M $NaCH_3COO/NaClO_4$ (pH 5.6), bovine carbonic anhydrase (BCA) was eluted. The eluates were collected as parts of 5 mL by a fraction collector. The flow rate was adjusted to 20 mL/h, and it was conducted at a temperature of 10-15°C.[10]

Protein Determination

For finding amount of pure enzyme, after scanning at 280 nm the tubes with significant absorbance were pooled and a quantitative protein determination was performed using the Coomassie Brilliant Blue G-250 method.[10]

Sodium Dodecyl Sulfate-Polyacrylamide Gel Electrophoresis

The purity of the enzyme was determined by applying a discontinuous sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE) (3%-10%) as reported by Laemmli.[11]

Determination of Hydratase Activity

Enzim aktivitesinin CO2'yi HCO3-'e dönüştürmesini ölçmek için, 2 mL veronal tampon (pH 8,2), 0,4 mL bromotimol mavisi (%0,004), 0,8 mL seyreltilmiş enzim çözeltisi (1/10 seyreltme) ve 2 mL doymuş CO2 çözeltisi 0°C'de karıştırıldı. The time t_c (for the sample) interval was determined between the addition of CO_2 solution and the occurrence of a yellow-green color. The same interval was recorded without enzyme solution (for blank). The activity was calculated from the following formula[12]:

1 WA Unit: $(t_o - t_c)/t_c$

Determination of Esterase Activity

At the same time, CA has esterase activity. This activity can be used for biosynthesis reactions. For this purpose, its activity was measured in this way. The principle of this determination is that the substrate of CA (*p*-nitrophenylacetate) is hydrolyzed to *p*-nitrophenol and acetic acid (Figure 2). The reaction is determined at 348 nm. For this procedure, 1.5 mL of a buffered enzyme solution (0.1 mL enzyme + 1.4 mL 0.05 M Tris–SO_4, pH 7.4), and 1.5 mL of substrate were mixed in a measurement cuvette, and 3 minutes later, the absorbance was measured (348 nm, 25°C). A blank measurement was obtained by preparing with adsorption support material without adding enzyme solution.[13]

Monitoring of Enzymatic Bio-mining

For this examination, 2 reaction vessels (1.74 mg/mL) containing 5 mL of the enzyme at pH 0.05 M Tris–SO_4 were used. In addition, in preparing the blank experiment, only 5 mL (pH 0.05 M Tris–SO_4) buffer was added to the 2 reaction cup. At last, 0.2 g Balkaya lignite coal was added to the vessels. Shaking and mixing effects were also investigated by using a shaker and a magnetic stirrer.

The samples were taken in a reaction mixture to understand the changing of the particle size of Balkaya lignite coal periodically. The size of the samples was measured with a light microscope after these recording images were compared and averaged.

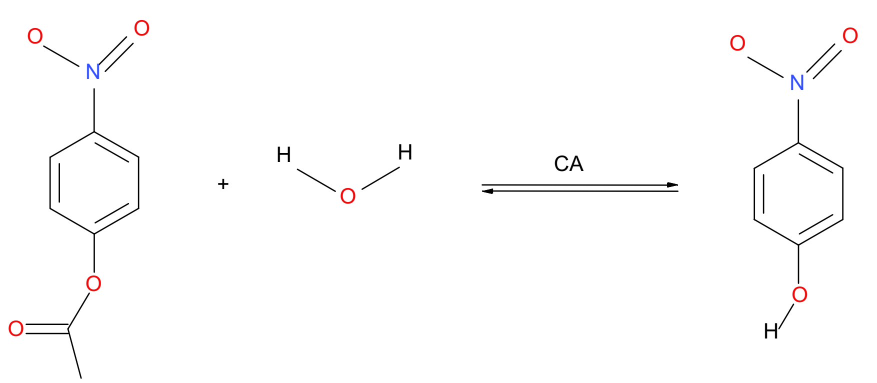
Table 1. Size Reduction (%) of Balkaya Lignite Coals Using Record of the Light Microscope

Size Reduction (%) of Mixed Enzyme Solution	Size Reduction (%) of Mixed Blank Solution	Size Reduction (%) of Shaken Enzyme Solution	Size Reduction (%) of Shaken Blank Solution
80	6.25	4	2.25

RESULTS AND DISCUSSION

Carbonic anhydrase was purified by Sepharose-4B L-tyrosine sulfanilamide affinity chromatography abundantly from bovine erythrocytes. The purity of the enzyme was determined by SDS-PAGE.

According to the results of the experiments using a shaker, the coal size was reduced 2.25 times in blank solution and 4 times



4-nitrophenly acetat

4-nitrophenol

Figure 2. Esterase activity of carbonic anhydrase.

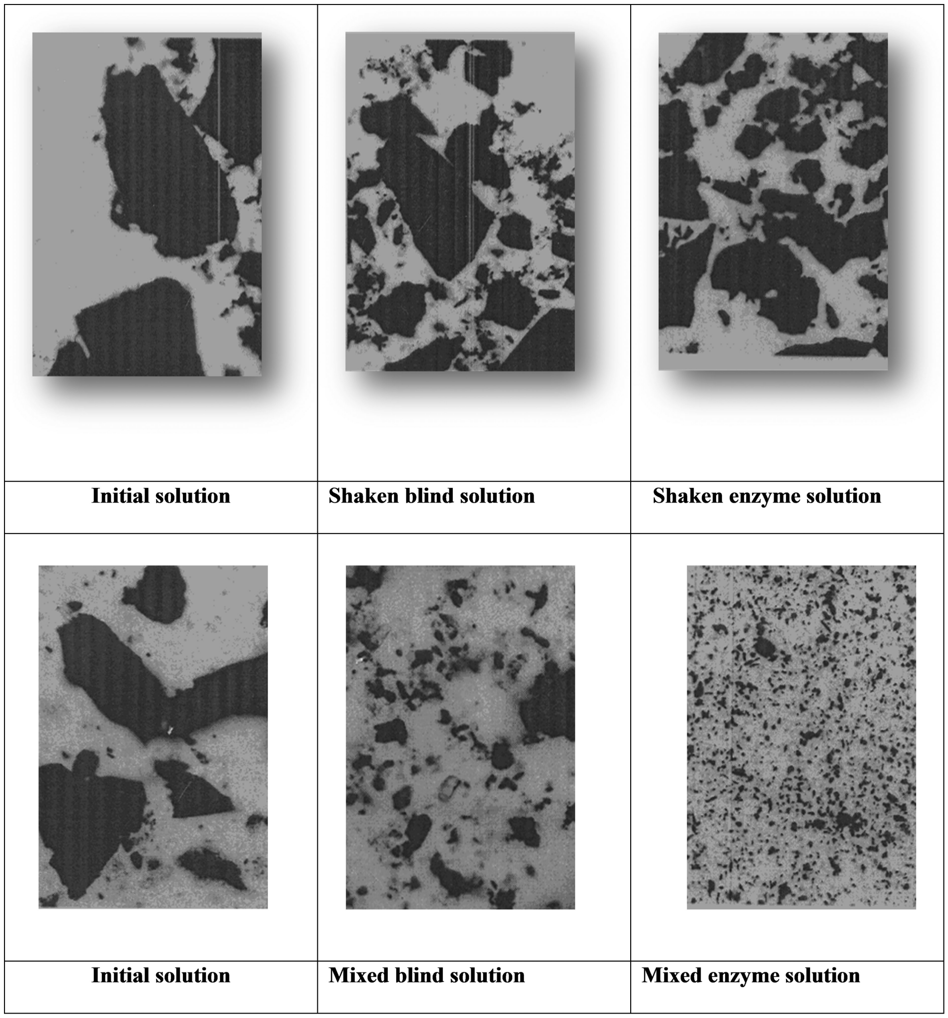


Figure 3. Records of scanning electron microscope (SEM-Jeol 6400).

in enzymatic solution. A shaker was used and the results were compared. It was observed that the minus effect of the enzyme could be seen in 96 hours. In addition, a magnetic stirrer was used and it was observed that the coal size was reduced 6.25 times in blank solution and 80 times in enzymatic solution in 96 hours (Table 1).

Evaluation of the results of enzyme activity to ensure the necessity of using a mechanical mixer was understood (Figure 3).

After enzymatic fragmentation, separation capabilities of dispersion particles were observed. The Balkaya lignite coal was estimated to become maseralls at the level of fragmentation by CA enzyme.

In addition, it was suggested that the BCA enzyme catalyzed the following reactions for coal decomposition using the esterase and hydratase activity of this enzyme (Figure 4).[14]

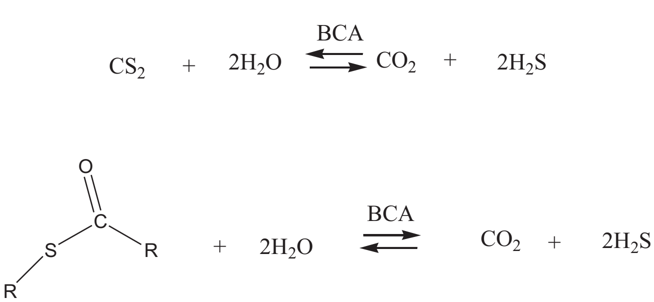


Figure 4. Two different activities of bovine carbonic anhydrase (BCA).

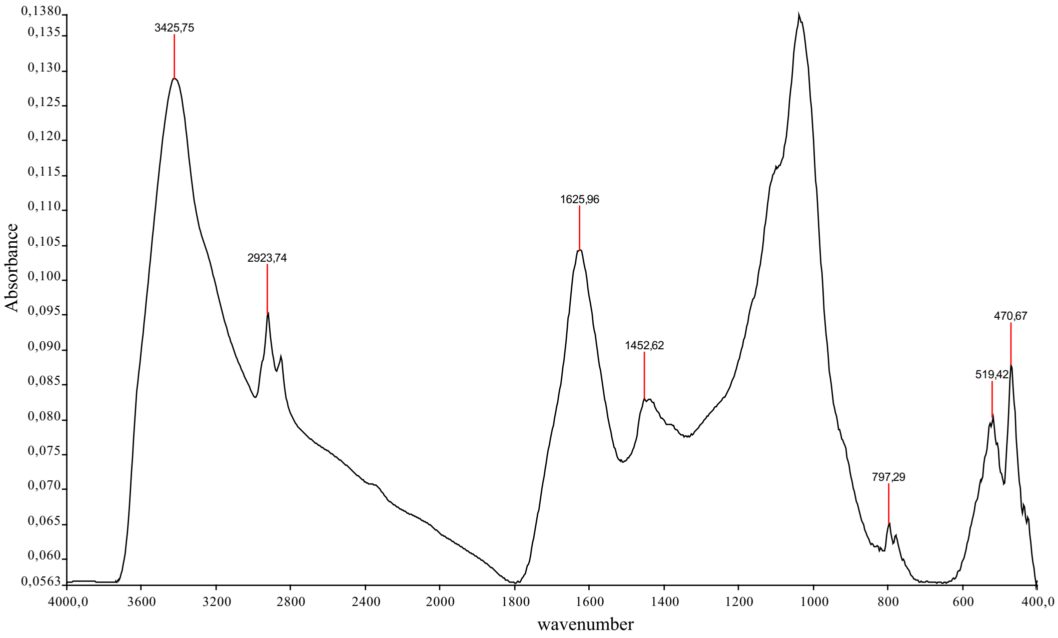
A dried blank and enzyme mixture including Balkaya lignite coal was used to understand whether the enzyme was changed to the structure of the Balkaya lignite coal. . The elemental analysis results are shown in Table 2. The results showed significant changes in the amount of %S and %C of coal structure.

From these results were considered the BCA used the Balkaya lignite coal as a substrate. Decreasing the %S and %C can be explanation of the occurring CO_2 and H_2S which is the results of upper reactions. These analyses were made with LECO CHNS.

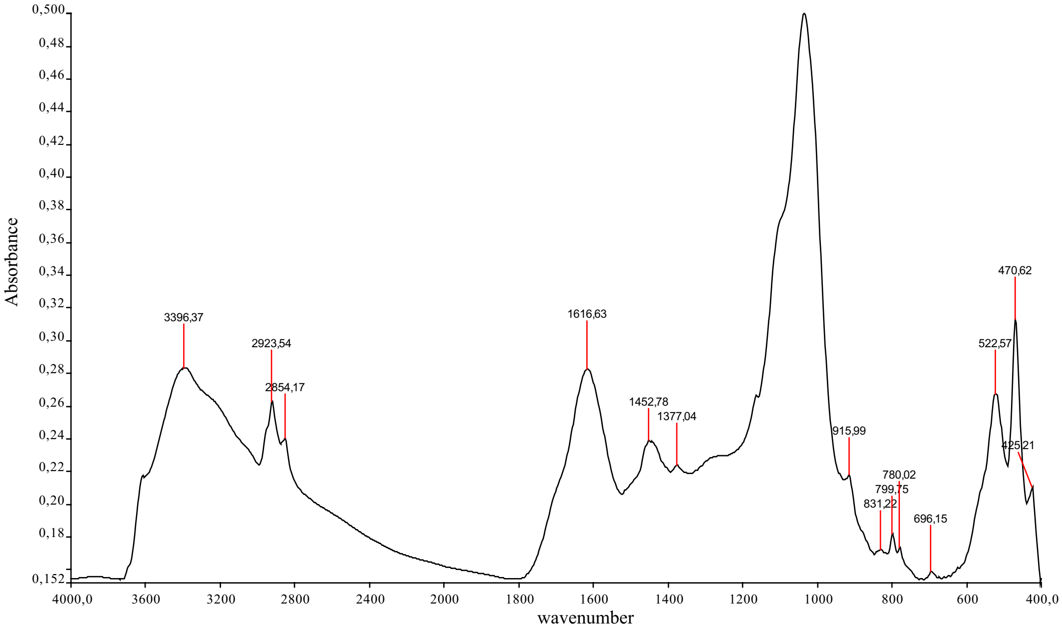
The Balkaya coal, reducing 73.75 times by bovine carbonic anhydrase, was analyzed using an infrared spectroscopy. The FTIR

Table 2. Elemental Analysis of Balkaya Lignite Coal

Dried blank solution including Balkaya lignite coal	C = 38.08%	H = 3.81%	N = 1.367%	S = 2.341%
Dried enzyme solution including Balkaya lignite coal	C = 21.18%	H = 3.962%	N = 1.285%	S = 0.985%



IR(KBr, cm^{-1}): Balkaya lignite coal: 3425.74, 2923.74, 1625.96, 1452.62, 797.29, 519.42,470.67.



IR(KBr, cm^{-1}): Enzymatic disintegrated Balkaya lignite coal: 3396.37, 2923.54, 2854.17, 1616.63, 1452.78, 1377.04, 915.99, 813.22, 799.75, 780.02, 696.15, 522.57, 470.62, 425.21.

Figure 5. The results of the IR spectroscopy.

spectroscopy results show all the different structures, as shown in Figure 5; for this analysis, Fourier-transform infrared spectroscopy (FTIR) spectrophotometer was used. Infrared spectra were obtained from solution in 0.1 mm cells or KBr pellets on a regular instrument.

FTIR analysis of the parts of the coal structure has been understood as a structural change due to enzymatic reaction. Therefore, the broken Balkaya coal compared with Balkaya coal of the fingerprint region of the spectrum shifts for observing changes in the coal structure.

CONCLUSION

Carbonic anhydrase enzyme is abundantly found in natural life. Therefore, it can be easily purified and characterized. In addition, CA enzymes can be easily purified from bovine blood. In this research, we understand that using this purified CA enzyme can be grounded in Balkaya lignite coal. The structural chancing of the Balkaya lignite coal was measured using light microscopy, elemental analysis, and IR spectrum. According to all the data obtained, it was determined that the structure was completely changed. Results of these experiments, CA enzyme can be used for bio-mining of the same kind of lignite coal.

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