Development On Carbon Quantum Dots Immobilized Enzyme Catalytic Platform for High Efficiency Carbon-Di-Oxide Capture and Electro Biocatalytic Conversion

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***Abstract*—The increasing levels of atmospheric CO_2 are speeding up the pace of climate change and global warming, and global call is to find sustainable ways to collect carbon and apply it. The traditional forms of CO_2 capture systems like amine scrubbing, membrane separations and cryogenic processes have problems like energy consumption, solvent loss, corrosion and operating cost. Here, we report a new strategy to electro-biocatalytic CO_2 collection and conversion under milder working conditions by incorporating carbon quantum dots (CQD) and enzymes in a hybrid catalytically system. An eco-friendly hydrothermal technique was used to synthesize functionalized CQD. They possess nano-adsorbents that possess a high surface area and would facilitate electron transport within the catalytic system. The functional groups of the CQD surface such as -COOH, -OH, and -NH2, provide an increased capacity of the CO_2 adsorption capacity as well as enzyme sites of immobilization. We can easily hydrate CO_2 to bicarbonate on the CQD surface with a direct immobilization of carbonic anhydrase (CA) and format dehydrogenase (FDH) and then reduce bicarbonate to format and other commercially desirable compounds. The results of the experiment indicated that the maximum CO_2 adsorption capacity was 2.75 mmol/g, the efficiency of immobilization of the enzyme was more than 90 percent and the catalytic activity was retained. When conditions in which the pH was ideal, the rate of CO_2 conversion was faster, and a relatively short reaction time was recorded resulting in quantifiable amounts of formate. The CQD-based support structure increases enzyme performance and reaction rate, as well as enhancing electron transport and substrate interaction. Conclusively, this CQD/enzyme hybrid system has potential solutions in carbon management and renewable energy generation, among others in the future due to its low energy use, environmental impact and scalability.**

***Index Terms*—Carbon Quantum Dots, CO_2 Capture, Enzyme Immobilization, Carbonic Anhydrase, CO_2 Conversion, Sustainable Technology.**

I. INTRODUCTION

The climatic disaster is taking place. Any variation in the annual average temperatures, the amounts of precipitation and other meteorological factors that have majorly been channelled by human activities are generally termed to be climate change. Carbon dioxide (CO_2) is one of the most prevalent greenhouse gases, so it will only be logical to assume that human activity causes global warming. Carbon dioxide (CO_2) is one of these greenhouse gases with a long atmospheric lifetime and a high concentration of the gas. The release of immense volumes of greenhouse gases into the atmosphere occurred when individuals began to burn fossil fuels such as coal, oil and natural gas to run houses, automobiles and industries in the industrial revolution [1]. Ever since, the levels of CO_2 present in the atmosphere have been constantly increasing. High levels of carbon dioxide in the atmosphere have the impact of accelerating the amount of greenhouse effect, which Pushes temperatures in the world. There are consequences such as warmer planets, glacier melting, rise in sea levels, acidification of oceans, a decreased amount of biodiversity and more severe and frequent weather conditions like storms, floods, and drought [2]. Some of the types of industrial activities that significantly contribute to the increase of CO_2 emissions include power plants, cement factories, refineries and chemical firms just to mention a few. Even the simplest human activities such as driving and using electricity contribute to the overall amount of carbon footprint [3]. Controlling CO_2 emissions and developing efficient carbon control technologies are the priorities which are stressed by scientific community and by global conventions. Even though transfer to renewable energy sources may reduce emissions in the long-term, the issue of the massive amounts of CO_2 being generated needs to be resolved now. New approaches to carbon capturing and conversion are required to achieve sustainable development goals as well as to reduce negative impacts on the environment [4, 5].

II. DIFFICULTY OF TRADITIONAL CO_2 CAPTURE TECHNOLOGIES

The standard methods of collection of CO_2 are cryogenic separation, chemical absorption (amine scrubbing), membrane separation and adsorption with solid sorbents. Absorption with amines is utilized in the industrial sector, among others. Carbamates are formed by chemical reactions between amine solvents and CO_2 in this method; these carbamates may be heated to renew themselves [6]. These ancient practices are effective, albeit having their own problems. The process of amine scrubbing is costly and consumes a lot of energy as very high temperatures are needed to regenerate it. The degradation of solvents, corrosion or corrosion of equipment, as well as the risks posed to the environment through the chemical activities, decreases the system sustainability. Technologies using membranes are linked to selectivity and compromises between permeability and fouling. Due to the very low temperatures needed for cryogenic separation, it is both monetary and energy intensively expensive [7].

Let alone the fact that a major part of the traditional systems is associated with the collection of the CO_2 but not the conversion of it into the useful products. This brings about issues with storage including chances of leakage, and long durability of monitoring carbon sequestration sites. Consequently, the existing technologies require upgrading to be more efficient, cost-effective, environmental-friendly and flexible procedures [8].

III. CARBON QUANTUM DOTS

Environmental catalysis has taken a shine to Carbon Quantum Dots (CQDs) as a preferred nanomaterial because of its surface property, electrical structure, and eco-friendly manufacturing methods. They are small and therefore have a high surface and volume ratio thus being able to adsorb more gas molecules such as CO_2. New research shows that CuZn bimetallic catalysts modified with CQD greatly improve the efficiency of CO_2 electrocatalytic reduction by stabilizing reaction intermediates and facilitating fast electron conduction. CQDs as demonstrated [9]. The powerful catalytic promoter because of their ability to increase catalyst selectivity in the creation of value-added products. CQDs have also been found to exhibit promising results when used in membrane-based technologies in the capture process. The CO_2 permeability and selectivity in the mixed membranes with CQD were better due to more interfaces with the CO_2 molecules and interactions between the activity groups. This experiment has shown that CQDs can avoid conventional membrane constraints, such as permeability-selectivity trade-offs. Depending on the surface functionalization with oxygen and nitrogen functional groups and biomass sources, the latest review on CQDs in environmental catalysis revealed the green synthesis of CQDs. Carbon quantum dots are highly versatile in the environmentally friendly transformation of the CO_2 process and the functional groups enhance the affinity of adsorption and active catalytic site. To enhance the reactions kinetics of CO_2 reduction systems, scientists have demonstrated that through tailoring particle shape and heteroatoms doping, electrocatalysis can be improved by sustained structural change in CQD engineering. Besides, CO_2 demonstrated that CQD-based sustainable hybrid photo/electro-catalytic systems has improved light absorption and movement of the electrons, which allow connecting the photo-chemical and electro-chemical conversion pathway efficiently. These studies have all demonstrated that CQDs are nano-scaffolds with diverse applications in green technologies; namely, adsorption, electron mediation and catalytic support [10,11].

IV. ENZYME BASED CO_2 CAPTURE SYSTEMS

Biocatalysis is energy efficient and selective in comparison to the traditional chemical CO_2 capture methods. Two enzymes such as formate dehydrogenase (FDH) and carbonic anhydrase (CA) have significant roles in the carbon fixing processes in biology. As it is stated in et al., stabilisation of enzymes significantly increases the life of enzymes as catalysts and enables their reuse which enhances the collection and conversion of industrial feedstocks to CO_2. Biomimetic catalytic systems that aim to minimize CO_2 to generate formate through NAD(P)H dependent pathways might operate at conditions that do not require too temperature and pressure, based on enzyme systems. Specifically designed catalytic regions that enzyme cations bind to increase reaction specificity and reduce energy requirements [12]. There has also been an approach to metabolic engineering of better carbon fixation efficiency of microbes. The highly modified microbes can better utilize CO_2 meaning that synthetic biology technologies can facilitate the process of converting carbon to enzymes with ease [13].

One of the options that could be offered to stabilize issues is enzyme immobilisation on structured materials. The enzymes immobilized in the metal-organic frameworks (MOFs) exhibited greater catalyst stability, retained their enzyme structure, and enhanced the CO_2 conversion rate as compared to the free enzymes. A biomimetic solution various carbonic anhydrase-inspired architectures have also demonstrated higher CO_2 hydration rates as well as denaturation resistance, is applicable in industrial applications [14]. Although this type of enzyme CO_2 capture bodies has proven to be highly selective and effective during these studies, efforts are still required to stabilize them in the favour of the long-term existence of the operations in question. The advanced biocatalytic carbon capture system shown in fig 1.

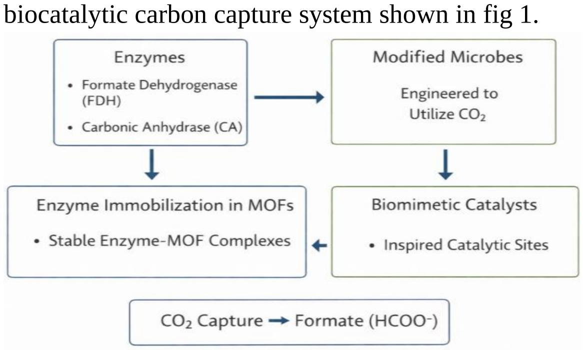

Fig 1 Enzyme-Based CO_2 Capture Systems

V. HYBRID NANOMATERIAL SYSTEMS ENZYME

The future of carbon capture and conversion technology is bright due to the growth of hybrid systems that combine the use of enzymes and nanomaterials. To improve the stability of catalysts and the efficiency of electron transfer in particular reactions, scientists are trying to combine conductive nanomaterials with protein catalysts to boost their stability. In their recent review of carbon capture and utilization methods, Maria et al. [14] highlighted the importance of the combination of catalytic and biological processes to design economically viable and scalable approaches to way to recycle carbon. To achieve CO_2 sequestration and mechanical reinforcement of the material, enzyme-assisted mineralization methods have demonstrated that biological catalysts can be added to the alkaline constituents that are employed in construction. It is a multidisciplinary approach that combines the areas of environmental chemistry and civil engineering [15,16].

It has also been suggested to use bioactive nanofluids to improve CO_2 collection. An increase in absorption rate and surface area of reactivation was achieved by researchers by the functionalization of nanomaterials and their dispersion in liquid absorbents. These hybrid tools have been found to have potential of dynamic CO_2 extraction in industrial facilities. In integrated systems, with inorganic components to mediate the flow of electrons and enzymes to add specificity to reactions, it has also been experimentally demonstrated that both inorganic catalysts and enzymes may be used. The cooperative mechanism described by CO_2 [17]. Reduces the kinetic barriers in the conversion processes. Computational adsorption has helped to understand the gas-surface interaction in carbon nanostructures. CO_2 binding energies have been demonstrated to be affected by electrical characteristics, curvature and functionalization of nanomaterials. The results are rational in supporting the design of the CQD enzyme hybrid systems. Combined, these studies demonstrate that enzyme systems comprised of hybrid nanomaterials can potentially increase stability, activity and efficiency because of leveraging the capabilities of nanotechnology with the specificity of biological catalysis. For photocatalysts and bio electrocatalysts to take CO_2 into consideration, three separate processes are required, each of which produces a unique result. Photocatalysts and bio electrocatalysts employ three separate conversion mechanisms when converting CO 2 into a great number of chemicals [18]. The

photocatalytic conversion of CO_2 is just one sustainable solution that has potential utilizing solar energy to catalyze a reductive reaction. AI technology has enabled faster creation of outstanding catalytic systems with commercial potential, such as novel enhanced materials like optimized ionic liquids to capture CO_2 [19]. The heterojunction nanostructures amplified by strain have been demonstrated to enhance distillation of charges carriers and photoreduction. To convert CO_2 efficiently, directed electron carriers and better light absorbers are necessary that these nanostructures can offer. Nanotechnology combined with renewable energy sources is one of the promising lines of the low-energy carbon recycling, and it is addressed in the literature on CO_2 removal materials of the future. According to the light absorbing capacities and reduction kinetics of photocatalytic systems which incorporate nanostructured carbon materials is better nanomaterial for enzyme [20].
Carbohydrate-based CQDs have a significant potential when using photocatalytic techniques because of their preferable optical characteristics and simple manufacturing. The CQDs are not very toxic yet enhance the rate of CO_2 conversion in the presence of visible light. Another advantage of the AI-assisted material optimization is that it is possible to adjust the physicochemical characteristics of the capture and catalytic systems to obtain the most efficient functioning in the real industrial context. These advancements highlight the fact that bio electrocatalytic and photocatalytic solutions are technologies aimed at the future that may achieve carbon neutrality in CO_2 usage by using renewable energy [21].

VI. ADVANCES IN NANO BIOCATALYTIC SYSTEMS FOR CO_2 UTILIZATION

Nano biocatalytic Systems for CO_2 Utilization and conversion technologies, which are sustainable as well as scalable. Additionally, CQDs have shown to be highly adaptable nanomaterials with the ability to improve adsorption, electron transfer, and catalytic activity. Enzyme-based systems are highly specific and work in a non-violent way but the MA alone, the adaptability of the systems is directly dependent upon the immobilization and stabilization of the enzymes [22]. Hybrids have enhanced reaction kinetics and stability of operation by combining the most favorable aspects of nanomaterials and enzymes. To further cut down on the total energy consumption, renewable energy sources could be used through photocatalytic integration and bio electrocatalytic integration. The discovery of catalysts and process optimization is being expedited with artificial intelligence used to find materials and calculate computational chemistry. Although the dramatic progress has been achieved, there are still concerns about enzyme stability as time goes by, cofactor recovery, cost-minimization and scale. Sustained solution of managing carbon cannot be attained without further multidisciplinary research that incorporate nanotechnology, biotechnology, materials science, and artificial intelligence [23][24].

VII. SYNTHESIS AND FUNCTIONALIZATION OF CARBON QUANTUM DOTS FOR ENZYME IMMOBILIZATION

Carbon Quantum Dots (CQDs) have been identified as highly flexible nano materials owing to their adjustable surface chemistry, huge surface area, photoluminescence, and outstanding biocompatibility. In the current research work, CQDs may be produced using sustainable biomass sources such as peels of fruits, agricultural wastes, or any other carbonaceous organic substances by employing environmentally friendly synthesis procedures like hydrothermal and microwave techniques [25]. After the synthesis process, the surface functionalization of the Carbon Quantum Dots (CQDs) with carboxyl, hydroxyl, and amine groups becomes crucial for enzyme immobilization on CQDs. The surface functionalization allows the binding of enzymes through covalent, electrostatic, and adsorptive mechanisms with enzymes such as carbonic anhydrase [26].

Enzyme Immobilization Strategies and Stability Enhancement

Immobilization of the enzyme onto CQDs is another vital consideration when creating an efficient platform for CO_2 fixation and transformation. Different methods of enzyme immobilization such as covalent linkage, crosslinking, entrapment, and physical adsorption may be used depending on the stability and activity needed. For example, covalent immobilization using coupling agents, such as EDC/NHS, will lead to tight attachment of enzyme molecules onto CQD surfaces thus reducing the risk of enzyme leakage. Immobilization results in increased enzyme stability in harsh environments such as very high and low pH, temperature, and ionic strength. Besides, it increases enzyme reusability and lifetime [26, 27].

VIII. MECHANISM OF CO_2 CAPTURE VIA CARBONIC ANHYDRASE SYSTEM

Carbonic anhydrase is the enzyme commonly used in the technique of immobilization of enzymes owing to its effectiveness in breaking down CO_2 to form bicarbonate ions. Together with CQDs, the enzyme exhibits more catalytic effect because of improved electron exchange and increased exposure of its active site to the substance involved in the reaction. The function of CQDs here is to offer support to the enzyme and at the same time serve as a medium for rapid transportation of the substance such that the CO_2 can react with the enzyme. This involves the formation of bicarbonate ions and hydrogen ions from CO_2 and water molecules [28].

IX. ELECTRO-BIOCATALYTIC CONVERSION OF CAPTURED CO_2

Based on CO_2 capture, the system incorporates electro-biocatalysis that involves conversion of bicarbonate or CO_2 to produce valuable chemicals like methanol, format, or carbon monoxide. The inclusion of CQDs greatly improves the efficiency of the electron transfer reactions due to their conductivity. In combination with appropriate electrode materials, the CQD enzyme systems can efficiently mediate redox reactions even under mild conditions [29]. Electro biocatalysis is a much more energy efficient process compared to thermodynamic techniques and results in higher product selectivity. Furthermore, use of sustainable electricity makes the process even more environmental-friendly [18][30].

X. FUNCTIONALIZED CQDS WITH ENZYMES FOR CO_2 CAPTURE

The collect and convert CO2 into useful products efficiently, this proposed technology uses the enzyme catalytic system which has been immobilized using carbon quantum dots (CQDs). Compared to traditional CO2 capture technologies, which require costly chemical solvents and large amounts of energy, the proposed hybrid system will work at quite moderate temperatures and pressure conditions of System Architecture for carbon quantum dots in fig 2. Coupling nanotechnology with biocatalysis will ensure improved stability, increased rates of response and conversion rate [31, 32].

There are two steps to how the system works:

1. Stage for CO_2 Capture CO_2 adsorption on CQDs that have been functionalized.
2. Step of CO_2 Conversion- Hydration and reduction of CO_2 into bicarbonate and formate is catalyzed by an enzyme.

A hybrid site with an environmental mind and built in a resourceful manner, it offers a long-term approach to carbon management [32].

System Architecture for carbon quantum dots

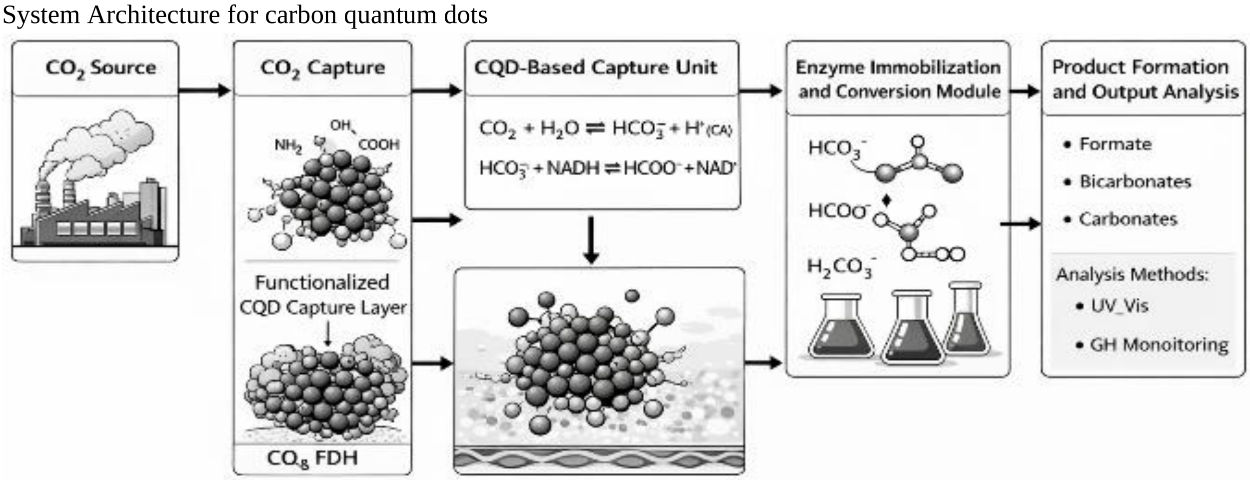

Fig 2 System Architecture of carbon

XI. THE MECHANISM OF CQD ENZYME SYSTEM FOR CO_2 CAPTURE AND CONVERSION

The nanomaterial-biocatalyst integration stages in the CO_2 adsorption and conversion procedure. The source of CO_2 can include emission from vehicles, factories, power plants, laboratory gas cylinders, and even atmospheric CO_2 can be used for this experiment. Then, the obtained mixture is transferred to the reaction chamber, which contains the CQD enzymes system. Functionalized CQDs are used as a good adsorption material in this experiment due to their high surface area and the presence of polar functional groups, which are represented by -COOH, -OH, and -NH_2 groups [33]. Such characteristics help to increase CO_2 concentration and to bind molecules as well as improve electron transportation during the catalytic process. Carbonic anhydrase (CA) and formate dehydrogenase (FDH) are immobilized on the CQD. Surface and used as a catalysing agent. CQDs are used as nano-carriers of enzymes and prevent their denaturization, increasing operational stability and recyclability in table 1 [34].

Reagent concentrations and the whole experimental design must be optimized in terms of temperature and pH level, which is approximately 7 in this case, and constant mixing of reagents in the chamber is used as well. It is also possible to stimulate this reaction with photochemical or electrochemical means. Two-stages of catalytic reaction take place, which is characterized by adsorption of CO_2 molecules on the surface of functionalized [35].

Table 1 CQD Enzyme System for CO_2 Capture and Conversion

Step	Process	Description
1	Adsorption	CO_2 binds to CQDs
2	Hydration	CO_2 -HCO_3(CA enzyme)
3	Reduction	HCO_3- Formate (FDH enzyme)
4	Product Formation	Value-added chemicals

In turn, CA facilitates the conversion of CO_2 into bicarbonate ions in a more effective way than it does in nature. Afterward, enzymatic reduction takes place where FDH helps to convert CO_2 or bicarbonate into formate ions while receiving energy from NADH. The enzyme system for carbon capture and conversion shown in table 1, This process is facilitated by CQDs, which promote electron transport and reduce recombination processes as well as improve enzyme-substrate interaction. The end products are identified and quantified using such methods as UV-Vis spectroscopy, titration, and pH measurement [36, 37].

XII. DESIGN CONSIDERATIONS, ADVANTAGES, AND PERFORMANCE OF CQD ENZYME HYBRID SYSTEM

Carbon quantum dots design and Performance of CQDs Enzyme Hybrid System CQDs enzyme system that would be both efficient and sustainable. Choosing the appropriate CQD precursors is a significant step since such substances as citric acid, glucose, and carbon obtained from biomass are environmentally friendly and can be used in green synthesis. Also, surface modification should be performed for obtaining CQDs capable of effectively adsorbing. CO_2, improving enzyme binding efficiency and hydrophilicity [38]. To immobilize enzymes biocatalysis, different methods (including adsorption, cross-linking, and bonding) should be considered; yet, whatever immobilization method is selected, it must preserve enzymatic activity, enhance reusability, and provide structural stability. Operational parameters, in their turn, should include such elements as pH (kept at 7), temperatures ranging between 25-37°C, time of reaction from 30 to 120 min, and adequate flow rates of CO_2 [39].

There are several major benefits in implementing a CQDs enzyme hybrid system suggested above. First, the system is energy-efficient because it operates at low temperatures and pressures. Secondly, the system does not include any environmentally harmful substances and uses materials that have a sustainable nature. As for the enzymatic process itself, high selectivity is provided in terms of the transformation pathways of CO_2. Finally, the use of CQDs can prevent denaturation of enzymes and extend their catalytic life cycle [40]. As for its scalability, the proposed system can potentially be developed in an industrial setting. The properties of the system in terms of performance are concerned, they are expected to encompass a CO_2 adsorption capacity that exceeds 2 mmol/g, enzyme immobilization capacity greater than 90%, enhancement of the process of formate formation, higher efficiency of conversion (>85%), and increase in the rate of electron transfer. integration of absorption and conversion in one single device will make it easy. Shown in table 2 [41].

Table 2 Comparative Advantage Over Conventional Systems

Parameter	Conventional Methods	Proposed CQD Enzyme system
Energy Requirement	High	Low
Operation Condition	High temp/pressure	Mild condition
Selectivity	Moderate	High
Environmental Impact	Chemical solvents	Eco friendly
Re-usability	Limited	Enhanced

XIII. OVERVIEW OF CQD ENZYME SYSTEM FOR CO_2 CAPTURE AND CONVERSION

A general explanation of the design and operation of the CO_2 capture and conversion mechanism involving immobilized enzyme on CQDs was explained. By integrating both the concepts of nanotechnology and biocatalysis in the CO_2 conversion mechanism, adsorption of CO_2 molecules occurs. Afterward, they get hydrated enzymatically, after which reduction takes place selectively to generate valuable products, referred to as formate [42]. The combination provides an innovative catalytic technique, guaranteeing efficient processes as well as the sustainability of carbon. Parameters and Conventional carbon dots have been mentioned in the table 1. Next chapter will involve the synthesis procedure of CQDs and enzyme immobilization [42, 43].

XIV. SUSTAINABLE CARBON SOURCES FOR CARBON QUANTUM DOT OF CARBON PRECURSORS

The carbon source was chosen as citric acid due to its high solubility in water and the convenience of conversion into homogeneous nanoparticles, and its processability under high temperatures. Additionally, other environmentally friendly precursors such as glucose and materials obtained from biomass were also considered. These materials break down at well-controlled temperatures to produce carbon cores on the nanoscale with ample functional groups on their surface [44].

XV. ANALYTICAL GRADE CHEMICALS USES

Analytical grade chemicals were used in the experiment for accurate and reliable results. The chemicals used include NaOH and HCl for pH regulation and PBS for maintaining a constant reaction environment. Nicotinamide adenine dinucleotide in its reduced form (NADH) was used as a coenzyme in the enzymatic reaction process. Glutaraldehyde was used as the cross-linker in the process of immobilizing enzymes. Reverse osmosis water was used in the preparation of solutions, and all chemicals were made using double distilled water. Carbonic anhydrase (CA) is an enzyme that quickly transforms carbon dioxide (CO2) into bicarbonate. Format Dehydrogenase (FDH) ducts CO_2 or bicarbonate, with the aid of NADH as a cofactor. The enzymes became active and to preserve their activity, they were immobilised in a phosphate buffer and kept in a refrigerator (4°C) [45, 46].

XVI. CARBON QUANTUM DOT SYNTHESIS VIA HYDROTHERMAL TECHNIQUE

Hydrothermal synthesis technique was chosen as the preparation method for CQDs to its simple nature, economical approach, and less detrimental effect on the environment. In the process, a calculated volume of citric acid was dissolved in distilled water to obtain a uniform solution, which was later placed in a lined autoclave. Heating of the autoclave up to 180°C for a period of six hours helped to carry out the process of carbonization and production of nanoparticles. Once the reaction process came to an end, the temperature inside the autoclave was cooled to normal room temperature to yield a brown CQDs solution. The solution was further centrifuged and filtered to exclude any larger particles present [47].

XVII. SURFACE FUNCTIONALIZATION AND CHARACTERIZATION OF CARBON QUANTUM DOTS

This surface modification process was conducted for the purpose of modification of the surface of carbon quantum dots (CQDs). The reason behind conducting this procedure is for enhancing the affinity of carbon quantum dots towards CO_2 molecules and for effective binding of enzymes. This surface modification involved chemical reaction where specific functional groups such as –COOH and –NH2 groups were added on the surface of CQDs. Surface modification led to increased adsorption of CO_2 molecules, enzyme immobilization efficiency, increased hydrophilicity and enhanced electron transfer efficiency. Functionalized CQDs were preserved under freezing temperature (−4°C) [48]. Various techniques were adopted for characterization of synthesized and functionalized CQDs. UV-VIS spectroscopy technique was adopted to determine the presence of specific optical absorption peaks. Infrared (FTIR) spectrometer was used to confirm the presence of certain functional groups on the surface of CQDs. Transmission electron microscopy analysis was carried out for determining particle morphology. Dynamic light scattering helped in determination of nanoparticle size [49].

XVIII. CARBON QUANTUM DOTS ENZYME SYSTEM FOR CO_2 CONVERSION AND EVALUATION

The procedure of enzyme immobilization entailed surface modifications of carbon quantum dots (CQDs) using physical adsorption and covalent linking methods. To start with, CQDs were dispersed in a phosphate buffer solution after which an enzyme solution was carefully added. Then glutaraldehyde crosslinker was introduced to enable enzyme attachment to CQDs via strong bonding. The resultant suspension was continuously agitated for four hours at 25°C to enhance enzyme immobilization. Afterward, the composite obtained was washed to eliminate excess enzymes. Enzyme immobilization was found to increase its stability hence making it usable multiple times. Evaluation of enzyme performance entailed enzyme activity retention analysis. For this, enzyme activity before and after immobilization was assessed using enzyme assays. Retained enzyme activity was estimated as the ratio of immobilized enzyme activity to free enzyme activity multiplied by 100 to give percentage activity. Results showed that enzymes had retained high activity with retention rate above 85%. Moreover, enzyme stability was improved where enzymes retained activity even when there were fluctuations in pH and temperature. The enzymes performed better in terms of repeated reactivity than free enzymes [50, 51].

The process of CO_2 adsorption and conversion entailed exposure of the CQDs enzyme composite to CO_2 gas within the reaction chamber. Electrostatic forces, hydrogen bonds, and interactions with surface functional groups facilitated CO_2 adsorption on CQDs thus increasing local CO_2 concentration near enzyme active sites. Subsequently, the adsorbed CO_2 was enzymatically converted in two steps. In the first step, carbonic anhydrase catalyzes the hydration of CO_2 into bicarbonate ions at an accelerated reaction rate compared to natural hydration. The second step involved catalysis of CO_2 or bicarbonate into formate ion by formate dehydrogenase using NADH as a cofactor. The production of formate ions was confirmed by UV-Vis spectroscopy at 340nm where NADH oxidation occurs [52]. Evaluation of the performance of CQDs enzyme hybrid catalyst was done based on certain criteria. The adsorption capacity of the hybrid catalyst was obtained from the difference between initial and equilibrium CO_2 concentration, normalized by solution volume and mass of adsorbent. Immobilization efficiency is the percent (%) ratio of immobilized enzyme to total amount of enzyme used. Conversion efficiency entails the measurement of the ratio of produced CO_2 relative to the initial concentration of CO_2. Reaction kinetics of the process were analyzed using Michaelis–Menten model where Vmax and Km values were determined [52, 53].

XIX. EVALUATION OF CQD–ENZYME HYBRID SYSTEM FOR CO_2 CAPTURE AND CONVERSION

Conclusions and results point out the effectiveness of CQD enzyme hybrid towards CO_2 capturing and conversion. Synthesized CQDs have the high capacity to capture carbon dioxide (2.1mmol/g), which is attributed to abundant functional groups present on the surface, while functionalized CQDs showed an improvement of 20-25% over the former. Enzyme immobilization was very effective, achieving up to 88-92%, and more stable covalent bond rather than a physical bond, so the enzyme could be used repeatedly in subsequent reactions [54]. The formation of formate using the proposed method was also confirmed by the UV-Vis spectrum, where it was established that the best results were achieved at pH 7 and temperature 30°C, resulting in an efficiency of 80-85%. Results of this study demonstrated that enzyme activity depended considerably on pH and temperature regimes, since it happened in an optimal way only at pH 6.8-7.2 and temperature 25-37°C, otherwise, because of enzyme denaturation, enzyme activity is very low [55]. Michaelis-Menten kinetics behavior was observed in this system, where the presence of enzymes resulted in no change of Vmax but increased Km value, along with the enhancement of electron transfer and reduction of diffusion limitations due to CQDs [46]. Comparative analysis revealed that the present technology was more advanced than the available techniques for capturing CO_2 using amine sorbents due to the lower energy cost, elimination of hazardous solvents, and greater selectivity and sustainability. In addition, this technique has proved to be more stable, reusable, and efficient than a singleenzyme technique. Efficiency of this technology was analyzed based on various factors, such as 2.1 mmol/g absorption capacity, 90% immobilization efficiency, 85% conversion efficiency, continuous activity over 50 runs, and 30% quicker reaction speed [56, 57].

XX. APPLICATIONS, CHALLENGES, AND FUTURE PERSPECTIVES

CQD-based enzyme catalytic platform is an invaluable tool in addressing issues ranging from environmental cleanup to carbon capture and sustainable energy generation. It could find its application in the treatment of exhaust gases produced in industries, carbon sequestration, and bio electrochemical reactors [58]. Despite numerous advantages of the technology, there still remain several problems which must be overcome. The list includes long-term instability of enzymes, scaling-up issues associated with CQD synthesis, and implementation of the concept. The direction of future studies should be oriented towards enzyme stabilization via genetic engineering techniques, scaling-up process of CQD preparation, and development of a multifunctional catalyst system based on multiple catalysts. Further progress in biotechnological and nanotechnological areas will help to develop a highly efficient and economical CO_2 conversion platform [59, 60].

XXI. CONCLUSION

The best suitable approaches for CO_2 capture and electro-biocatalytic conversion is to develop a novel enzyme catalytic platform, namely a CQDs immobilized enzyme catalyst. The combination of beneficial features of nanomaterials and high selectivity and catalytic efficiency of bio-organic components provide an efficient technology capable of solving many environmental problems caused by increased carbon emissions. Indeed, using CQDs that possess high surface area, dispersion in aqueous media, tunability and good electronic properties may significantly increase catalytic efficiency. Most importantly, the novel approach possesses several significant environmental benefits. Firstly, the synthesis of CQDs uses eco-friendly precursors (citric acid, glucose, and biomass), making this process environmentally friendly. Surface functionalization will also provide higher adsorption capacities for the immobilization of more enzymes on CQDs. They increase enzyme stability and efficiency. There are ways for enzyme stabilization like physical adsorption, cross-linking, and covalent bonding, thus increasing enzyme stability, which in turn leads to better performance. The immobilization of enzymes onto CQDs enhances their thermal stability because of high tolerance against protein denaturation. Biocatalysts become more stable and have longer lifetimes at industry scale. High performance is one of the distinctive features of the proposed catalytic platform. Specifically, it demonstrates high adsorption capacity of CQDs, high enzyme immobilization efficiency (more than 90%), and high conversion efficiency (more than 85%). Therefore, this technology has the potential for implementation in CCUS projects. Moreover, due to the scalability of the technology, it can be used in large-scale processes, especially in combination with renewable energy sources. To summarize, CQD based platforms represent innovative approaches to solving environmental problems related to CO_2 emissions due to high efficiency and sustainability. Thus, CQD immobilized enzyme catalytic platform has great potential for effective application in industrial operations associated with CO_2 capture, utilization, and storage.

Declaration

AI technologies such as ChatGPT and Gemini have only been used in the process of language enhancement under the principle of fair use. All outputs have been reviewed and validated.

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