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Review

Application of Nanofluids in CO_2 Absorption: A Review

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Abstract: The continuous release of CO_2 into the atmosphere as a major cause of increasing global warming has become a growing concern for the environment. Accordingly, CO_2 absorption through an approach with maximum absorption efficiency and minimum energy consumption is of paramount importance. Thanks to the emergence of nanotechnology and its unique advantages in various fields, a new approach was introduced using suspended particles in a base liquid (suspension) to increase CO_2 absorption. This review article addresses the performance of nanofluids, preparation methods, and their stability, which is one of the essential factors preventing sedimentation of nanofluids. This article aims to comprehensibly study the factors contributing to CO_2 absorption through nanofluids, which mainly addresses the role of the base liquids and the reason behind their selection.

Keywords: CO_2 capture; nanofluid; absorption; improvement; solvent

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1. Introduction

The European Union (EU) has long term strategies to reduce carbon-based energy systems till 2030 and 2050. This energy strategy is set to reduce Greenhouse Gas (GHG) emissions, increase the efficiency of energy systems, and gradually substitute fossil fuels with renewable energy sources (RES). One of the targets is to reduce carbon emissions by about 40% by 2030 [1]. CO_2 is the main greenhouse gas and constitutes about 77% of the emissions all around the world. The emission of an excessive amount of CO_2 intensifies global warming. Fossil fuel burning and the production of cement are the two main CO_2 emitting sources [2]. One way of decreasing the emission rate of CO_2 to the atmosphere is its separation and collection, utilization, or storage for further application. There are several separation methods to capture CO_2 from various gas streams. Adsorption, absorption, cryogenic, and membrane separation are the main technologies used in CO_2 capture [3,4]. Much progress has been made in CO_2 absorption by gas-liquid, some of them are proposed to reduce the energy demand. The gas-liquid absorption technique can also be applied to other renewable energies for the absorption of carbon dioxide. Typically, the novel absorption methods that use solvents benefit from physical and/or chemical phenomena to improve the absorption process. This technique has higher efficiency in low concentrations of CO_2, therefore it has a better performance in separating CO_2 from the flue gas mixtures of post-combustion processes that contain low concentrations of CO_2 [5]. The probable chemical absorption mechanism of CO_2 is that one NH_2 group attacks CO_2 with the free electron pairs of its N atom and as a result, a hydrogen bond is formed with another NH_2 group. The chemical absorption of CO_2 in flue gas by a solvent is a selective and reversible chemical reaction. One of the major challenges is to minimize the energy demand of this process [6].

Many different solvents have been used for CO_2 chemical absorption so far. The selection criteria of a suitable solvent are: fast kinetics of the reaction; high capacity of absorbent; low regeneration energy demand; and low rate of solvent degradation [7]. Today, amine solvents are the most widely utilized chemical solvents for CO_2 capture. The reasons are their high capacity, high thermal stability, and the high reaction rate of amine solvents with carbon dioxide molecules [8]. The sterically hindered amines and simple alkanolamines are the two major types of amine absorbents. Monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) are primary, secondary, and tertiary amines that are classified as simple alkanolamines. All amine absorbents are different in some respects, such as stability, absorption capacity for CO_2, the kinetics of reaction with CO_2, and corrosion products. MEA is considered the standard amine solvent for carbon dioxide absorption; the reason being the high efficiency (90%) of CO_2 capture, fast kinetics, high mass transfer rate, and capability of CO_2 absorption even at atmospheric and low pressures of flue gases [9]. Nevertheless, since absorption of CO_2 with chemical solvents containing amines is a mature and economically feasible method, that can be used on large scale to treat flue gas streams with high volumes, it has been at the center of attention in recent years [10,11]. This method also has some drawbacks including high energy demand for solvent recovery, expensive materials, weak performance in selective absorption from acidic gases, corrosivity, the occurrence of side reactions, and resultant water-saturated gas, and being detrimental to the environment [12,13]. CO_2 absorption processes with the physical solvents Selexol and Rectisol need high-pressure conditions and are governed by Henry's law. Despite chemical absorption, there is no need for heat in physical absorption, and the solvent is recovered by pressure reduction in these processes [14–16]. However, physical solvents have some drawbacks; they are sensitive to the partial pressure of acid gas (acid gas partial pressure should be high), they hardly meet H_2S specifications, the concentration of inert gases must be low [14]. Some of the commonly used physical solvents are NMP (N-Methyl-2-Pyrrolidone), DEPG (Dimethyl Ether of Polyethylene Glycol), and PC (Propylene Carbonate) [17].

The cryogenic processes is another CO_2 absorption process that takes advantage of the intrinsic properties of components of a gas mixture; CO_2 capture is done using the distinct desublimation and condensation properties of CO_2 and its carrier gas. The high purity of CO_2 (99.99%) is achieved in a highly efficient (99.99%) process, compared to other CO_2 capture techniques [18]. In this process, a CO_2 phase change occurs in flue gases, after several stages of compression and cooling. Other constituents of the mixture will invariably experience phase change, too. CO_2 might be separated as a liquid or a solid along with other components and can be further purified by distillation. However, the absorbent pores are at risk of blockage by the water from other components, and in this case, the cost of CO_2 capture will increase [19]. One of the commercial gas separation and purification processes is membrane separation. This highly efficient, environmentally friendly technique is utilized in some gas purifying systems like natural gas sweetening and air separation and can compete with the other absorption systems for CO_2 removal from flue gas [20]. The concept of membrane separation is very simple. Nevertheless, in the case of post-combustion capture, some membrane properties like permeability and selectivity, limit its utilization. As an example, 95% purification of CO_2 with a 90% CO_2 capture rate is not feasible with a single-stage membrane. When talking about using membrane separation in gas-transport pipeline systems for CO_2 capture, we face two conflicting effects, high energy consumption in low membrane areas and high investment cost for large membrane areas [21].

Adsorption is a promising alternative to chemical adsorption processes; the process in which one or more components are removed by attachment to a solid surface is called adsorption. The basis of adsorption is the intermolecular interactions between solid materials surface (like activated carbon or molecular sieve) and the adsorbed gas (like CO_2). Single or multilayer adsorption depends on the variables of the partial pressure of the absorbed gas, temperature, adsorbent pore sizes, and surface forces [22]. Activated carbon, metal–organic frameworks, zeolites, and microporous organic polymers are solid absorbents that have some superiorities in CO_2 adsorption capture. The lower energy consumption of CO_2 capture by adsorption is attracting increasing attention. Gas streams with different CO_2 content can be treated with temperature vacuum swing (TVS), vacuum swing adsorption (VSA), temperature swing adsorption (TSA), electrical swing adsorption (ESA), and pressure swing adsorption (PSA) [23].

In addition, there are other processes for CO_2 absorption, such as Ionic Liquids (Ils), electrochemical conversion, photochemical, thermochemical, and biochemical, using organic/metallic (organometallic) catalysts on chemical and hybrid rings. Even though all of these methods are promising in CO_2 absorption, they are still being evaluated with respect to the obstacles pertinent to cost, energy, and also their application at large scales [24,25].

Over the recent years, CO_2 absorption through nanofluid has captured interest due to its unique advantages in adjusting physical and chemical properties and its special applications and high specific area. Due to their porosity, nanomaterials, such as nano-sized zeolites, metal, and metal oxide nanoparticles, metal-organic frameworks (MOFs), covalent organic frameworks (COPs) promisingly increase the efficiency of CO_2 absorption [26].

This article is a comprehensive review of the summary of the last advances in nanofluids in increasing CO_2 absorption. In addition to describing nanofluids, properties, and applications, this study also elaborately introduces the factors contributing to increasing CO_2 absorption. In the following, the nanofluid preparation methods consisting of one-step and two-step methods will be explained. Afterward, nanofluid stability, mechanisms of increasing mass transfer in nanofluids (shuttle effect, bubble breakage effect, and micro convection), and the factors affecting CO_2 absorption through the nanofluid will be discussed and summarized. Ultimately, based on the base liquid, nanofluids will be categorized into three categories (water, amine, and methanol), and a conclusion and viewpoint in reaching favorable CO_2 absorption in nanotechnology will be provided. By describing the application of nanofluid in the CO_2 absorption field, this article evaluates and helps understand this novel technology and compares it with conventional methods.

2. Nanofluid

Nanofluids are prepared by dispersing nanosized materials (nanotubes, nanoparticles, nanorods, nanofibers, nanodroplets, and nanosheets) in a base fluid [27]. Nano-sized materials are determined according to their strict definition that specifies materials with at least one dimension (length, diameter, or thickness) in the range of 1–100 nm. This definition is widely accepted by nanotechnology researchers. The origin of this definition comes back to the fact that when the particle size is decreased, the ratio of surface area to volume increases rapidly, therefore 100 nm was set as a criterion for nanomaterials. Nanofluids are typically prepared by dispersion of ceramics (PNP, aluminum nitride, cellulose, etc.), carbonaceous materials (fullerene, graphene, carbon nanotubes, etc.), metals (gold, copper, aluminum, etc.), and inorganic oxides (silicon dioxide, zinc oxide, iron oxide, etc.) in a base fluid [28]. A refrigerant, mineral oils, liquids with high viscosity like ethylene glycol, and low viscosity liquids like water, or a blend of various liquids (propylene/water, water/EG, etc.) may be used as base fluid.

The researchers found that the addition of nanoparticles to the base fluid led to changes in the thermophysical properties of the nanofluid. In other words, Nanofluids caused changes in the base fluid due to their unique thermophysical properties such as density, thermal conductivity, viscosity, and other thermodynamic properties. Table 1 summarizes some of the thermophysical properties of common nanoparticles.

Table 1. Properties of nanoparticles.

Nanoparticle	Average Particle Size [nm]	Morphology	Surface Area [m^2/g]	Density [kg/m^3]	Thermal Conductivity (W/m·K)	
Al_2O_3	<40	Spherical	-	4700	36–40	[24]
MWCNT	10–20	Tubular	200	2100	-	[29]
ZnO	10–30	Nearly spherical	20–60	5606	29	[30]
TiO_2	<50	Spherical	50 ± 15	5500–6000	-	[29,30]
SiO_2	10–15	Spherical	180–270	2200	-	[31]

Table 1. *Cont.*

Nanoparticle	Average Particle Size [nm]	Morphology	Surface Area [m^2/g]	Density [kg/m^3]	Thermal Conductivity (W/m·K)	
Fe_3O_4	4	Spherical	40–60	5200	17.65	[32]
CNT	10–20	-	332	1800	-	[33]
NiO_2	50	-	-	6670	-	[34]
MgO	-	Cubic	-	2900	48.4	[35]

Choi was the first one who proposed this definition for nanofluids in 1995 that two-phase, uniform and stable suspensions resulted from the dispersion of nanoparticles in an inorganic or organic liquid phase with a pre-specified proportion [36]. Nanofluids are theoretically classified as colloidal dispersion systems with properties that are related to the characteristics of the nanoparticles like shape, properties, scale, content, or their chemical or physical properties of nanoparticles [37]. Tests that have been carried out on nanofluids also indicated many beneficial points; when compared to particles with millimeter or micrometer sizes, nanofluids are more stable and have higher thermal conductivity, pressure drop and erosion are lower, especially in microchannels, when using nanofluids. Many industries benefit from nanofluids like the chemical industry, electronics and machinery, aerospace, biomedicine, energy, and power. Nevertheless, the application of nanofluids as mass and heat transfer media has attracted special attention due to their high mass and heat transfer coefficients [38,39]. These advantages of using nanofluids have made researchers eager to discover other fields of application of nanofluids.

Since mass transfer and heat transfer have similar basic principles, nanoparticles can also influence mass transfer by a fluid. Researchers concluded that using small quantities of soluble particles will considerably increase the gas absorption rate. The enhancement in mass transfer rate was later proved by Ruthiya et al., who assessed four probable mechanisms to improve mass transfer in gas–liquid systems [40]. Krishnamurthy et al., were one of the first groups that studied mass transfer improvement in nanofluids. They compared the diffusivity of fluorescein dye droplets in deionized water and a mixture of nanofluids in water [41]. Now, the focus of the studies is on using nanoparticles to increase the rate of absorption, mass transfer, and carbon loading in nanofluids [42]; this way, the resistance against mass transfer between liquid and gas phases will be decreased. The application of nanofluid as CO_2 absorbent could reduce the cost of energy in CO_2 capture systems by the enhancement of absorption rate. As an example, one way of reducing the energy consumption and cost of a CO_2 capture plant is to utilize nanographene oxide (NGO) nanofluids in CO_2 capture and sequestration (CCS) recovery that benefits from the gas hydrate formation process [43]. The dispersion of nanoparticles in an absorption solvent can improve the absorption performance due to the high surface area of these particles that creates Brownian motion, micro convection, and shuffle effects. The small size of nanoparticles also increase the rate and capacity of CO_2 absorption compared to the same particles with larger sizes [44]. However, if the concentration of nanoparticles exceeds the optimal point, nanoparticles will be agglomerated and prevent gas absorption into the liquid phase. Several gas absorption investigations were carried on using nanofluids while an external magnetic field was also applied to the gas absorption in a column [45]. In this respect, the convective mass transfer under the influence of nanoparticle dispersion in the fluid was also investigated in several liquid–gas absorption systems such as a tray and packed absorption column, wetted-wall column (WWC), gas–liquid hollow fiber membrane contactor, liquid–liquid extraction (LLE), gas-sparged stirred absorption vessel, bubble-type column absorber, and three-phase airlift reactor [46].

2.1. The Method of Nanofluid Preparation

Nanofluid preparation is the principal stage in experiments. However, the superb performance of a nanofluid highly depends on its method of preparation [47]. Nanofluids are not a simple dispersion of solids in liquids. Nanofluids should necessarily be stable, durable, and even suspensions with minor agglomerations that do not experience any chemical change of the fluid, etc. The agglomeration of nanoparticles is one of the main challenges of nanofluid preparation. Therefore, the formulation of a highly efficient CO_2 absorber nanofluid is a fundamental stage in the preparation of CO_2 absorption nanofluids. According to Figure 1, nanofluids are prepared using the (a) one-step method (Vapor deposition), and (b) two-step method (mixing) [48].

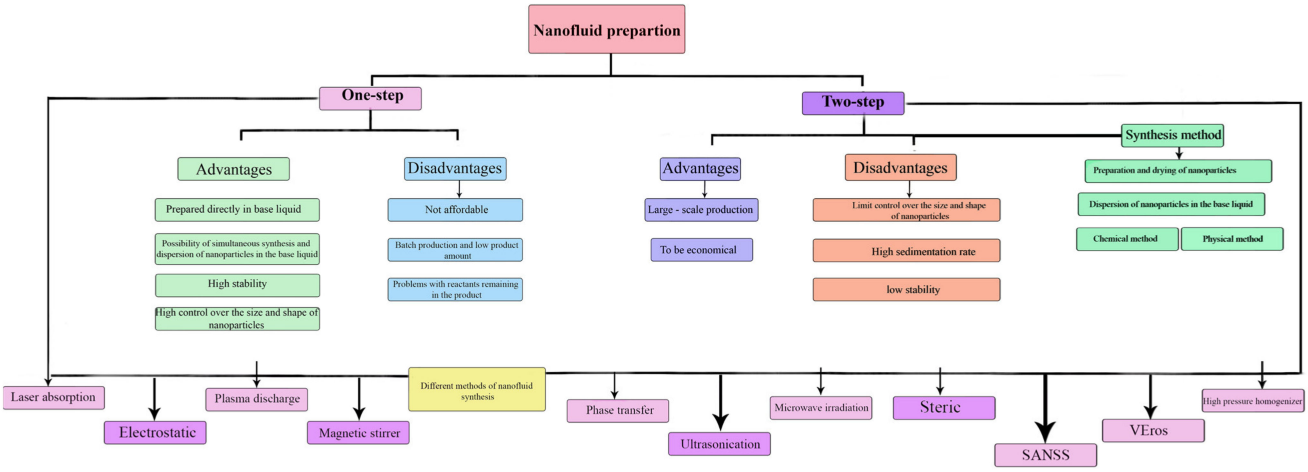

Figure 1. Different methods of preparing nanofluids.

2.1.1. One-Step Synthesis Method

In the one-step method, nanofluid is directly prepared in the base fluid and there is no need for intermediate phases like storage or drying of nanoparticles and their dispersion in the base fluid [49]. This means, the synthesis and dispersion of nanoparticles take place at the same time and inside the base fluid, this hinders oxidation of nanoparticles. Some technologies like plasma, microwaves, or lasers can help this process. Nanoparticles like Au, Ag and Cu have been successfully synthesized via a single-step method [50]. This process was also used by some researchers for the preparation of nanofluids. To prevent the agglomeration of nanoparticles, dispersion, drying, transportation, and storage are eluded in this method, this will increase the stability of nanofluid and lower the production costs. Generally, since single-step nanofluid preparation is a rather costly method, it is not practical in large-scale production. Thus, special focus has been placed on the single-step chemical process, which is a relatively cost-effective method of nanofluid preparation [49].

2.1.2. Two-Step Method

In this method, different nanopowder materials like nanoparticles, etc., are utilized by physical, chemical, and mechanical methods [51]. The direct method of application includes first the dispersion of nanoparticles in the base fluid and then using a stabilization method. Although the resultant nanofluids have small size nanoparticles with high surface activity, they easily agglomerate. Ultrasonic waves are utilized to increase the stability of the obtained nanofluid and yield a dispersible suspension of nanoparticles. Some of the advantages of the two-step method are the low cost, simple process, large-scale nanofluid preparation, and industrial realization [52]. However, the stability of the nanofluids prepared in this way is weak, and using surfactants is not applicable at high temperatures. Therefore, some dispersing methods such as using ultrasound vibration, the addition of surfactant, pH variation of the base fluid, and ultrasonication are combined in some cases, to reach a suspension with better dispersion performance [53]. Nevertheless, it is recommended that nanofluids containing oxide nanoparticles may better be prepared by a two-step process, while this method is not suitable for metallic nanoparticles [54].

2.2. Nanofluid Stability

Stability is a main problem of nanofluids. Van der Waals forces are the reason for the instability of nanofluids and are intensified by the increased number of nanoparticle collisions with each other due to Brownian movements, and the large surface area of nanoparticles themselves [55]. Nanofluids are susceptible to destabilization and leave deposits under the influence of gravitational force, electrostatic repulsive force, Van der Waals attraction, and buoyancy forces. The function of gravitational force and Van der Waals force is toward the destabilization of any colloidal suspension [56]. This means that these forces help the dispersed particles in adhering to each other and aggregates with bigger sizes will form as a result. These large particles will precipitate from the suspension under the influence of gravitational force and form deposits at the bottom of the container [57]. The settlement of the particles is due to their heavier weight that prevents Brownian motions maintaining the particles in a stable suspension. Based on theory, the main features that remarkably increase the conductivity of nanofluids and their stability are aggregation and clustering. However, this theory merely applies to specific groups of nanoparticles like single-wall nanotubes that have a high aspect ratio [58]. Therefore, destabilization of the nanofluid occurs as a result of the susceptibility of nanoparticles to form aggregates and clusters in the suspension. Accordingly, the two major stability aspects of nanofluids are nanoparticle aggregation and sedimentation.

In the past few years, some of the many attempts for the preparation of stable nanofluids were partially successful. Different methods have been utilized for the stabilization of suspended nanoparticles (colloids) in nanofluids [59]. Thus, it is necessary to investigate the stability of nanofluids for suitable utilization in proper applications. The determination of effective factors on the stability of nanofluids is also of great importance [60]. Generally, several techniques are used for the evaluation of nanofluid stability; some of them are spectral absorbance and measurement of transmittance, settlement and centrifugation, 3ω method, measurement of zeta potential, TEM (transmission electron microscopy), and DLS (dynamic light scattering [38]. In general, two methods can improve the stability of nanofluids, which can be divided into two major categories: Physical methods and chemical methods as shown in Figure 2.

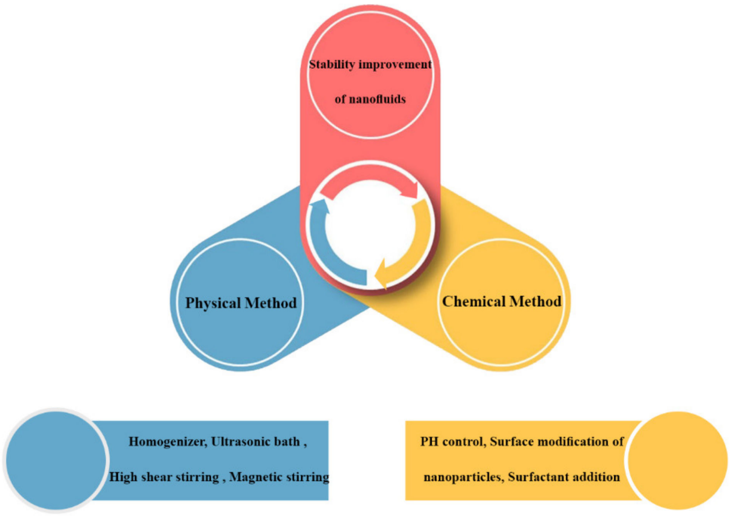

Figure 2. Methods for improving the stability of nanofluids.

2.2.1. Sedimentation and Centrifugation

The most commonly utilized method for stability assessment is sedimentation. The basis of this method is the settlement of nanoparticles out of the nanofluid under the influence of gravity [61]. The volume or weight of sediment is a good indication of nanofluid stability. If the concentration of supernatant particles remains unchanged over time then the nanofluid is considered stable [62]. The method deals with the observation of nanoparticle settlement from a nanofluid in a container over time. Generally, most papers have considered the stability time frame as the time during which obvious sedimentation does not occur, or at least negligibly occurs, in the nanofluid. Some researchers accepted the sedimentation method as a criterion for the assessment of the stability of a nanofluid [63]. But the sedimentation technique is not a time-efficient method [64]. To overcome this problem, researchers use the centrifugation method which is a more time-efficient method for the assessment of nanofluid stability. In this method, sedimentation is accelerated under the influence of centrifugal force which is much stronger than the gravitational force [65].

2.2.2. Zeta Potential

Another method of stability determination of a nanofluid is using the zeta-potential test in which mutual repulsion happens between nanoparticles with the same charge. Thus, there is little agglomeration tendency between the particles with high surface charge, in their collisions [66]. This method can help describe the differences in some experimental data, where the structure of the suspension and the nanoparticles' surface charges are altered by using surfactants [67]. The zeta potential technique is a basic test for determining nanofluid stability, which considers the electrophoretic behavior of the fluid [68]. According to the theory of electrophoresis, the zeta potential measures the repulsion force between two particles [69]. Based on the stabilization theory, a high value of zeta potential is an indication of a high solubility of particles in the suspension, which is due to increased electrostatic repulsion between particles [70]. It is suggested that suspensions with 5 mV zeta potential or less are not stable and experience agglomeration, those with 20 mV have limited stability, but the suspensions with >30 mV have physical stability and if their zeta potential is greater than 60 mV they will have excellent stability [71].

2.3. The Mechanisms of Enhancement in Nanofluids

Many research works have focused on the role of fine particles in the enhancement of mass transfer in gas–liquid systems. These findings indicated that partial pressure enhancement will give rise to the gas absorption capacity, meanwhile, temperature enhancement decreases the gas solubility in the liquid phase, which is in accordance with the ideal gas law [72]. The theory that suggests enhancement in mass transfer by using nanoparticles has not been established. Several mechanisms are accepted: micro convection; mixed boundary layer; bubble coalescence prevention; and the shuttle mechanism. The bubble breaking effect, shuttle mechanism, and micro convection are discussed in this paper as shown in Figure 3 [73].

2.3.1. Shuttle (Grazing) Effect

The shuttle effect was proposed by Kars et al., who discussed the rate enhancement of gas absorption in liquid in a gas–liquid-solid three-phase system when solid particles are present, using a theoretical model [74]. The grazing effect states that the gas absorption from liquid can be enhanced by using particles that can penetrate the gas–liquid mass transfer membranes to absorb a specific amount of gas [75].

Also, the shuttle effect considers that particles could enter the gas–liquid mass transfer membrane and absorb a certain amount of gas. And due to the concentration difference, particles carrying absorbed gas return to the bulk liquid and then desorb [76]. Owing to the strong adsorption of the diffusing gas phase component in the dispersed phase particles, the concentration of this gas-phase reactant in the liquid phase near the interface will be decreased, resulting in an increment in the absorption rate [77].

2.3.2. Bubble Breaking Effect

Krishnamurthy et al., have concluded that the velocity disturbance field is the reason for the enhancement of mass transfer, which is formed due to the movements of nanoparticles [41]. In the bubble absorption process, the collision of nanoparticles and nanoparticles with bubbles occurs. When the bubbles move toward the interface and form a dynamic movement, the nanoparticles strike the interface of gas–liquid and this results in breaking the bubbles [78]. This phenomenon increases the diffusion area. Considering that this enhancement in the specific interfacial area occurred due to the particles, it can be concluded that they can increase the overall mass transfer coefficient [79].

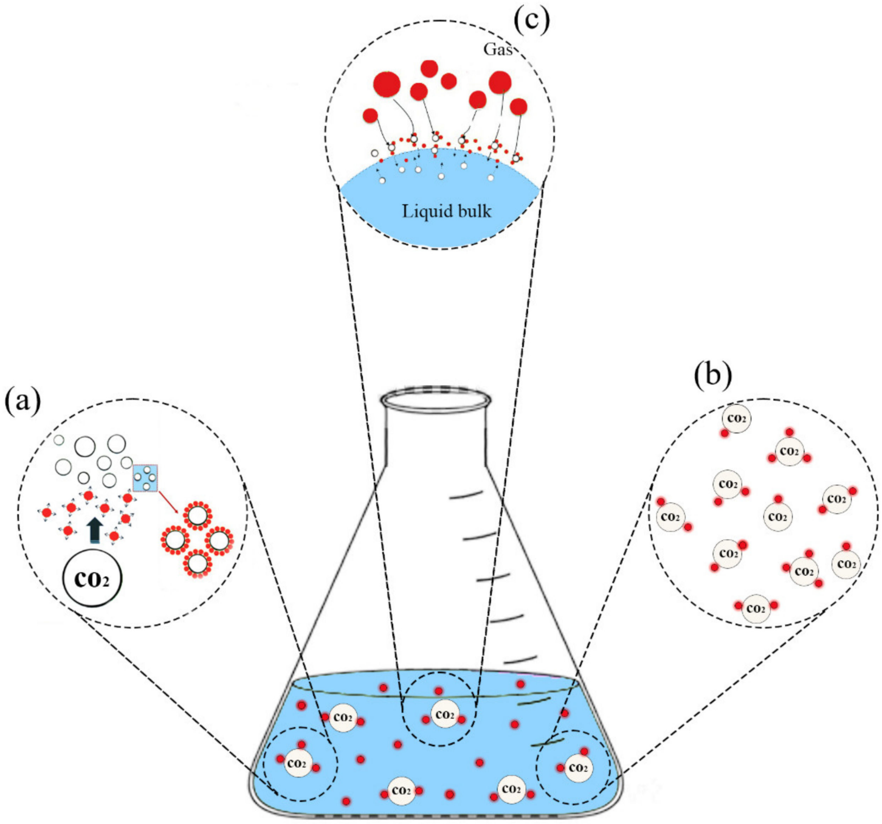

Figure 3. The schematic of (**a**) Bubble breaking, (**b**) Brownian motion, and (**c**) Grazing effect mechanisms in the improvement of CO_2 absorption.

2.3.3. Micro-Convection

The convective mass transfer process is strongly influenced by the Brownian motions and the resultant micro-advection near the particles that scatter a considerable fraction of the measured species molecules [80]. The solute diffusion can also be enhanced by micro-convection that is promoted by Brownian movements, this enhancement will also improve the diffusion coefficient. There is also a synergistic effect between the mass and heat transfer. When heat transfer is enhanced, changes in the gas–liquid phase temperature result in an enhancement in the potential for absorption [81]. The governing mechanism is that the micro-convection is enhanced by the fluid disturbance, the liquid disturbance is caused by random particle movement called Brownian motion [82]. The determination of the optimal nanoparticle concentration in a liquid depends on the Brownian motion that creates micro-convection. The mentioned three mechanisms play key roles in the enhancement of CO_2 mass transfer [83].

3. Effective Factors in the CO_2 Absorption by Nanofluid

Nanofluids' properties have opened a new research field in new technologies. Researchers started investigations on various nanofluids to be used as absorbents in CO_2 absorption processes. In this respect, different metal oxide, metallic, and nonmetallic nanoparticles were examined for CO_2 absorption enhancement; some of them are TiO_2, MgO, SiO_2, Cu, CuO, Al_2O_3, and carbon nanotubes [84]. The dominant parameters were determined according to the results of CO_2 absorption using nanoparticles. These factors are nanoparticle type, morphology, size, and concentration in the base fluid, flow rate of gas, concentration of CO_2 in the feed stream, and base fluid type, flow rate, pressure, temperature, and hydrodynamics as presented in Figure 4 [53].

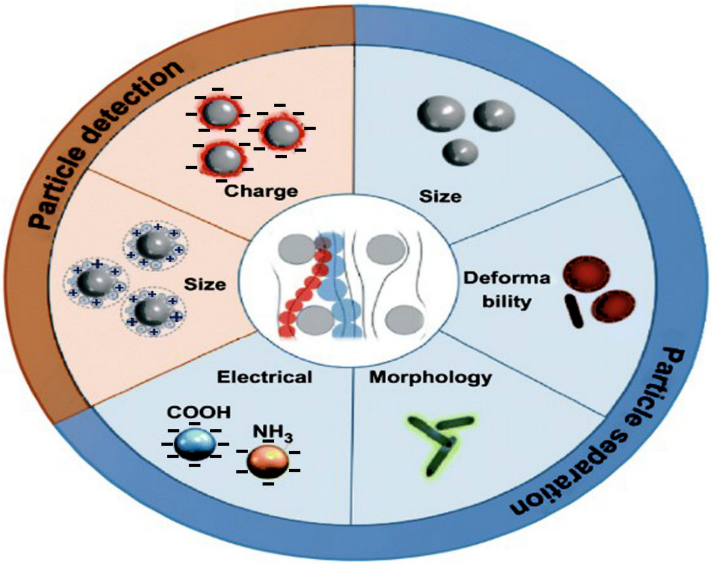

Figure 4. The main parameters of nanoparticles in CO_2 absorption.

3.1. Effect of Nanoparticle Type

Ganapathy et al., observed gas–liquid absorption enhancement when using nanoparticles in the form of nanofluids in bubbling absorption systems for CO_2 capture, which was different for each nanoparticle type. When equilibrium is reached in a gas–liquid absorption system, the gas concentration slightly increases in the liquid phase [85]. In a research study, Fang et al., used a bubbling ammonia system for the investigation of nanoparticles' effects on CO_2 absorption. The relationship between the type of nanoparticle and the efficiency of CO_2 capture was determined. The sequence of CO_2 capture efficiency was $TiO_2 > CuO > SiO_2$ [86]. The CO_2 removal efficiency of a stirred reactor containing CNT and Al_2O_3 nanoparticles was studied by Sumin et al. The results of their experiments indicated a considerably enhanced CO_2 capture when using carbon nanotubes in the absorption solvent [33]. In a study, Pineda et al. investigated the effect of TiO_2, SiO_2, and Al_2O_3 nanoparticle addition to the absorption solvent in a new annular contactor (AC) that utilized a tray absorber. This study suggested up to 5%, 6% and 10% enhancement in the absorption rate when using TiO_2, SiO_2, and Al_2O_3 nanoparticles, respectively [87]. Zhang et al., used a stirred reactor to examine the influence of TiO_2 nanoparticle addition into propylene carbonate, on the capture rate of the system; the effects of particle size and the optimum concentration of nanoparticles were also analyzed in their experiments [73]. Golkhar et al., used a gas–liquid hollow fiber membrane contactor to remove CO_2 with a nanofluid containing silica nanoparticles and carbon nanotubes. Their findings showed that CNT nanofluid has better performance in CO_2 removal with up to 40% efficiency [31].

3.2. Effect of Nanoparticle Concentration

In one investigation, an isothermal quasi-static high pressure stirred reactor was utilized to study the effect of temperature and concentration of ZnO and SiO_2 nanoparticles in water-based nanofluid on CO_2 absorption. Results indicated temperature enhancement slightly reduces the CO_2 absorption, whereas the addition of 0.1 wt.% ZnO and SiO_2 increases the CO_2 absorption by 14% and 7%, respectively [88]. The influence of MWCNTs addition to the CO_2 absorbent fluid was investigated by Nabipour et al., and the outcomes indicated that 0.02 wt.% concentration of MWCNTs with carboxyl functional groups in Sulfinol-M absorber results in a 23.2% enhancement in CO_2 equilibrium solubility compared to the base fluid [89]. CO_2 absorption in a bubble absorber system was studied by Kim et al., to evaluate the performance of a nanofluid containing SiO_2 nanoparticles on CO_2 absorption. The 0.21 wt.% nanofluid showed a 24% enhancement in CO_2 absorption performance compared to pure water as its base fluid [90]. Peng et al., investigated the effect of Ag nanoparticle addition into water/NH_3 mixture on the mass transfer performance of an absorption column, they found that the rate of CO_2 absorption was increased by 55% when 0.02 wt.% Ag nanoparticles were added to the solution [91]. Lee and Kang used a bubble column system to investigate the influence of Al_2O_3 nanoparticles addition to a NaCl solution on the CO_2 absorption performance of the system and observed that only 0.01 vol% of Al_2O_3 nanoparticles can improve the CO_2 solubility. All these investigations indicate that the addition of small amounts of nanoparticles to an absorption fluid can enhance its absorption capacity [92]. The CO_2 absorption capacity of a nanofluid containing Fe_2O_3 nanoparticles was recently investigated by Darvanjooghi et al. [93] and it was shown that the maximum mean CO_2 flux of 2.8×10^{-5} mol/(m^2.s) was achieved at a Fe_2O_3 concentration of 1 wt.%, which decreased after a while. The effect of HKUST-1 with polyethyleneimine functional groups was studied on the CO_2 absorption capacity of an aqueous solution of 40 wt.%. This study which was carried out by Irani et al., showed a 16% enhancement in CO_2 absorption capacity when only 0.2 wt.% nanoparticles were used [94]. Periasamy Manikandan et al., studied the influence of Al_2O_3 nanoparticles on mass transfer of a water-based nanofluid and reported the maximum CO_2 absorption enhancement at 0.6 vol% concentration of Al_2O_3 nanoparticle [95]. Huang et al. [96] and Park et al. [97,98] added SiO_2 nanoparticles to a solution mixture of MEA, DEA, and Diisopropanolamine to evaluate its performance in CO_2 absorption in a stirred cell. They witnessed a reduction in the CO_2 absorption rate by increasing the nanoparticle concentration, which is believed to be related to the elasticity of the solution [99]. According to these investigations, the addition of small amounts of nanoparticles to a fluid significantly enhances the CO_2 absorption of the nanofluid.

3.3. *Effect of Nanoparticle Size*

Many different types of nanoparticles were used in investigations of CO_2 mass transfer efficiency enhancement by the addition of nanoparticles to aqueous solutions as Al_2O_3, SiO_2, and TiO_2 nanoparticles [100,101]. Nagy et al., achieved more than 200% mass transfer enhancement by the addition of 10 vol% of n-hexadecane nanoparticles with 65 nm size into a fluid. According to the results, the rate of mass transfer increases rapidly at low concentrations of nanoparticles, whereas its enhancement is slow at higher concentrations of particles (more than 6 vol%) [102]. Lee and Kang, concluded that the addition of smaller Al_2O_3 nanoparticles to a NaCl solution shows higher enhancement in the CO_2 absorption capacity of the fluid [92]. Zhu et al., used an agitated microreactor to show the superiority of a nanofluid containing mesoporous silica materials (MCM41) with a mean particle size of 250 nm compared to micro-sized silica particles (1.4 and 7 mm), in CO absorption by water [103]. A study of the literature shows that Kim et al., were the only research group that studied the influence of nanoparticles on the mass transfer performance of nanofluids. They dispersed silica nanoparticles with average particle sizes of 30, 70, and 120 nm in water to reach a nanofluid with 0.021 wt.% nanoparticle concentration. Results showed up to 76% enhancement in CO_2 absorption of a nanofluid containing 0.021 wt.% nanoparticles, 24% of this enhancement occurred in the first minute of a total 8 min duration of the absorption process. These increases were 11% and 12%, respectively, for nanofluids containing K_2CO_3 nanoparticles. The conclusion of their investigation was the contribution of small bubbles that exist in nanofluids in the enhancement of mass transfer [90]. Huang et al. suggested that the improvement of volumetric mass transfer coefficient continues until the particle size reaches 60 nm, and a further increase in particle size does not affect the efficiency of nanofluid CO_2 absorption [96]. Generally, increasing the volume fraction of nanoparticles will increase the enhancement factor, while enhancement of nanoparticle size decreases this enhancement factor [47].

3.4. *Effect of Temperature*

Temperature also plays a key role in CO_2 absorption enhancement by nanofluids. Lee and Kang introduced a novel CO_2 absorbent consisting of a NaCl aqueous solution containing Al_2O_3 nanoparticles. They assessed the solubility of CO_2 in this nanofluid at different temperatures and concentrations of Al_2O_3. They reached 11%, 12.5%, and 8.7% enhancement in CO_2 capture at 30 °C, 20 °C, and 10 °C, respectively, when Al_2O_3 nanoparticle concentration was 0.01 vol% in the solution [92]. Another study carried out by Lee et al., that was carried out in a bubble reactor indicated that the rate of CO_2 absorption increased by 4.5% at 20 °C and Al_2O_3 concentration of 0.01 vol%; this enhancement was 5.6% when Al_2O_3 was substituted by SiO_2 nanoparticles at the same temperature [104]. Jung et al., achieved an eight percent enhancement in CO_2 absorption rate in a bubble reactor at Al_2O_3 nanoparticle concentration of 0.01% and 10 °C. These results imply that better mass transfer efficiency was obtained at lower concentrations of nanoparticles [105].

4. Classification of Nanofluids Based on Base Liquid

Determination of the most suitable solvent for CO_2 absorption is another challenge. A suitable solvent must be cheap with high availability, non-toxic, non-corrosive, non-flammable, and should have a low vapor pressure. Brine, water, ionic liquids, amines, alcohols, amines, and piperazine (PZ) are the most commonly used solvents for this purpose [106]. Three types of nanofluids named water mixtures, amines, and methanol are introduced in the following.

4.1. Amine-Based Nanofluid

Amine absorption of CO_2 is classified as a chemical process in which a gas–liquid phase mass transfer occurs. Absorption and desorption columns are used for this purpose. The gas–liquid equilibrium determines the absorption performance of the selected amine [107]. Amines have fast kinetics in CO_2 absorption. The water solubility is increased and the vapor pressure is reduced by the hydroxyl functional group in the amine, while the alkalinity is facilitated by the amino groups in an aqueous solution [108]. Accordingly, aqueous alkanolamine solutions are the most common solvent used in industrial gas sweetening processes in scrubbers.

Generally, the number of hydrogen atoms of an ammonia molecule substituted with other functional groups is the basis of the classifications for amines into three groups that are primary amines like MEA, secondary amines including DEA, and tertiary amines like MDEA; secondary amines have fast reactions with acidic gases like CO_2 with a higher rate of regeneration energy consumption in comparison to the tertiary amines [109]. The most commonly used amine solvent in large plants is the primary amine of MEA, which is highly reactive and is economically feasible. Nevertheless, this solvent is corrosive and requires a high amount of energy for regeneration.

Several MEA mixtures are proposed in the literature to reduce the energy consumption of this solvent; A mixture of tertiary amines with primary amines is often desirable [110]. The favorable acid gas loading of MEDA has made it a cost-efficient solvent for gas sweetening processes. This solvent has low corrosivity and needs lesser amounts of heat for regeneration. The problem is the weak selectivity of MDEA for CO_2 in the presence of H_2S. One way of increasing CO_2 selectivity is to activate it before being used in CO_2 separation processes; this activation can be achieved through some additives like PZ or MEA [84]. PZ is another attractive candidate for CO_2 absorption due to a higher reactivity than MEA. But, PZ has also some drawbacks such as higher volatility compared to MEA, higher cost-intensive implementation in CO_2 than MEA which is still in the development phase. Lots of papers are available in the literature that consider the efficiency, advantage, and disadvantages of amine solvents. For instance, AMP (2-Amino-2-Methyl-1-Propanol) is a primary amine with steric hindrance with higher CO_2 absorption capacity (due to bi-carbonate formation), furthermore, it is less corrosive compared with MEA.

According to the literature, CO_2 is soluble in aqueous solutions containing alkanolamines. This absorption can be further improved by the addition of PZ as an activator, similarly the additives can also enhance and accelerate the absorption of CO_2. On the other hand, since different species exist in different amines, the chemical stability and corrosivity of the products of CO_2 absorption will be different from one another. Corrosion causes some problems for the process including the reduction of equipment lifetime. Besides, the strong chemical bonds of amine solvents with CO_2 require high amounts of energy for the desorption process. This high energy demand of the solvent recovery process and corrosion of scrubbers used for CO_2 capture (water-based alkanolamine solutions) led to the idea of developing solid sorbents [10].

Many research studies suggested that the addition of promoters or the dispersion of a third phase such as solid particles, can considerably increase the gas absorption performance [33]. In other words, one way of increasing the rate of CO_2 absorption in CO_2 capture processes is to increase the CO_2 mass transfer. This mass transfer improvement can be achieved by the addition of fine particles to the solvent, which increases the rate of gas removal in gas–liquid mass transfer processes in the absorption columns, therefore, the equipment size will be reduced. It means that in the processes where CO_2 diffusion is involved, the acceleration of the absorption rate is achieved by the enhancement of mass transfer. Therefore, fine particles were added to the liquid phase to increase the mass transfer; it also increases the efficiency of gas–liquid absorption columns or decreases the required size of the equipment due to the enhancement in removal rate of the mass transfer process from gas to the liquid phase.

Thus, the substitution of amine solvents with amine-based nanoparticle absorbents that are dispersed in the liquid phase can save a significant amount of energy since these absorbents do not require high amounts of energy for heating and cooling cycles to recover the liquid solvent [111]. An overview of the recent works in the CO_2 absorption with amine-based nanoparticles is presented in Table 2.

Wang et al., used dispersions of Al_2O_3, SiO_2, and TiO_2 nanoparticles in MEA base fluid to be used in CO_2 capture processes. TiO_2 showed the highest improvement in CO_2 absorption [112]. Similar reports are available in the literature. Jiang et al. carried out some experiments to determine the effect of four nanoparticles of SiO_2, MgO, TiO_2, and Al_2O_3, on the improvement of CO_2 capture. They found that TiO_2-MDEA nanofluids have the best CO_2 absorption performance among the four solutions. Since TiO_2 has the highest CO_2 adsorption capacity, its solution shows the maximum absorption performance due to the higher gradient of CO_2 concentration that it provides in the solution. Furthermore, the CO_2 absorption performance of TiO_2-MEA nanofluid was better than TiO_2-MDEA nanofluid; the reason was the higher rate of the chemical reaction between MEA and CO_2 [105]. Hwang et al. [96] and Park et al. [97–99] studied the impact of SiO_2 nanoparticles addition to MEA, DEA, and DIPA aqueous solutions, on CO_2 absorption rate in a stirred cell. Results indicated that the enhancement of nanoparticle concentration reduces the absorption rate due to the solution's elasticity. The absorption enhancement performance of Al_2O_3 and SiO_2 nanoparticles were assessed when they were dispersed in three different base fluids of MDEA, PZ, and MEA. The coefficient of mass transfer measured at the liquid side indicated a significant enhancement in absorption kinetic of PZ absorbent after the addition of nanoparticles [113]. Komati et al., enhanced the absorption rate of CO_2 capture by amine solutions when nanoferrofluids were used as the enhancement agent. They indicated that the addition of 0.39 vol% of nanoparticles to the base fluid results in a 92.8% enhancement in the absorption capacity compared to the base fluid [99].

The utilization of a nanofluid mixture of graphene-Oxide/MDEA in the gas sweetening process was assessed by Irani et al. [114]. The addition of only 0.1 wt.% graphene oxide to the solvent could promote its absorption capacity by 9.1% which is attributed to the increased mass transfer coefficient due to the hydroxyl functional groups on the graphene oxide surface. In another study, Park et al., studied the impact of colloidal nanosilica addition to 2-amino-2-methyl-1-propanol solvent on CO_2 absorption performance in a stirred vessel. They found that as the concentration of nanoparticles increases the absorption rate and the volumetric mass transfer coefficient in the liquid side decreases [115]. Rahmatmand et al. [84] have also witnessed that the addition of CNT nanoparticles does not significantly affect the DEA absorption performance because DEA is a powerful chemical absorbent of CO_2. Nevertheless, CNTs could significantly enhance the absorptionn capacity of MDEA-based nanofluid for CO_2 capture.

In general, it can be concluded that absorption capacity increases by increasing nanoparticle concentration in the base fluid [89].

Table 2. Summary of various types of amine-based nanofluids.

Researchers	Base Fluid	Nanoparticle	Size of Nanoparticle (nm)	Contactor Type	Enhancement %	Absorbent Loading
Rahimi et al. [116]	MDEA	nMWCNT	11.6	Stirred reactor	141.6	0.05 wt.%
	MEA		11.6		20.79	0.1 wt.%
Jiang et al. [42]	MEA	TiO_2	20	Bubbling reactor	9	0.6 kg/m^3
	MDEA	TiO_2	20		30	0.4 kg/m^3
	MEA	Al_2O_3	20		4	0.6 kg/m^3
	MDEA	Al_2O_3	20		15	0.8 kg/m^3
Irani et al. [114]	MDEA	GO	29.3–35.16	Stirred cell reactor	10.4	0.2 wt.%
Taheri et al. [117]	DEA	Al_2O_3	10–20	WWC	33	0.05 wt.%
		SiO_2	10–15		40	0.05 wt.%
Irani et al. [94]	MDEA	PEI-HKUST-1	-	PSE	16	0.2 wt.%
Aghehrochaboki et al. [72]	MDEA	GO	-	Stirred cell reactor	10.4	0.2 wt.%
		PEI-GO	-		15	0.1 wt.%
Rahmatmand et al. [84]	MDEA	CNT	*	Batch vessel	23	0.02 wt.%
Pashaei et al. [118]	PZ	TiO_2	20	Stirrer Bubble column	14.7	0.05 wt.%
		ZnO	10–30		16.6	0.1 wt.%
		ZrO_2	20		3.7	0.05 wt.%
Li et al. [119]	MDEA	TiO_2	15	Stirred cell reactor	11.54	0.8 wt.%
Komati et al. [99]	MDEA	Fe_3O_4	15	WWC	90	0.39 vol%
Wang et al. [112]	MEA	Al_2O_3	15	Bubble Column	10	0.06 wt.%
		SiO_2	15		10	0.06 wt.%
		TiO_2	15		13	0.06 wt.%
Wang et al. [113]	MEA	Al_2O_3	20	WWC	7	0.02 wt.%
		SiO_2	15		10	0.06 wt.%
Elhambakhsh et al. [120]	MDEA	Fe_3O_4@SiO_2-NH_2	31–39	Stirred cell reactor	16.36	0.1 wt.%
		Fe_3O_4-proline	10–16		6.78	0.02 wt.%
		Fe_3O_4-lysine	13–18		12.13	0.1 wt.%
Jiang et al. [121]	TETA	SiO_2	45	Bubble reaction system	29	0.10 wt.%

*: Outside diameter = 8 nm, Inside diameter = 2.5 nm and Length= 10 µm.

4.2. Water-Based Nanofluid

Water as a non-toxic natural absorber can physically bond with CO_2 and H_2S. Some advantages of distilled water (DW) when being used as an absorber are its high surface tension and proper capacity for CO_2 absorption. Nevertheless, it has a weak performance in CO_2 recovery and has a low absorption rate [122]. Thus, many researchers suggested that dispersing nanoparticles in raw water can considerably increase gas absorption into the resultant nanofluid as depicted in Table 3.

For instance, the CNT-water was used by Ma et al., as a binary nanofluid for the absorption of ammonia. The experiment results indicated that a solution mixture of 0.23 wt.% CNTs in water yields a 16.2% improvement in the absorption of the fluid [123]. Periasamy et al., have dispersed copper and graphene nanoparticles in a solution mixture of water and ethylene glycol and reported a considerable improvement on the base fluid thermophysical properties [124]. A numerical investigation was carried out by Darabi et al. on the carbon dioxide adsorption by hollow fiber membranes using two different solutions of SiO_2/water and CNT/water. The CNT/water fluid had better performance compared to SiO_2 nanoparticles and its rate of CO_2 capture was 16% higher than the other solution. The reason is the lower adsorption capacity of SiO_2 nanoparticles compared to CNT nanoparticles [125]. The suspension of SiO_2 in water was also assessed from mass and heat transfer aspects and a significant enhancement was observed in mass and heat transfer rates that were 18% and 47%, respectively [126].

Komati et al., used magnetic nanoparticles to enhance the CO_2 absorption rate of the base fluid [99]. Salimi et al., used Fe_3O_4 and NiO suspension in water for the absorption of CO_2 in a packed bed. The results indicated an improvement in mass transfer performance of the nanofluid after the addition of magnetic nanoparticles in the CO_2 capture process [34]. Samadi et al., could achieve 22.35% and 59% enhancement in CO_2 mass flux and mass transfer coefficient just by using a wetted wall column for CO_2 absorption, which was equipped with an external magnetic field. The nanofluid that was used in their experiments was Fe_3O_4/water [127]. The Fe_3O_4 nanofluid was also examined by Darvanjooghi et al., for the CO_2 absorption in constant and alternating magnetic fields. The results indicated that high strength magnetic fields increase both mass transfer rate and solubility of CO_2. The results showed a maximum value of CO_2 solubility and the average molar flux of absorption into the nanofluid when an AC field was applied. They indicated that as the strength of the magnetic field increases, the renewal surface factor and CO_2 mass diffusivity in the nanofluid increase as well, while the thickness of the diffusion layer decreases [93]. Haghtalab et al., utilized a batch stirred vessel to study CO_2 solubility in SiO_2/water and ZnO/water nanofluids. The ZnO/water nanofluid showed better CO_2 absorption than the SiO_2/water nanofluid in their experiments. Furthermore, CO_2 absorption was examined by some researchers in membrane contactors with water as the absorption media. They found that the addition of some materials as promoters to deionized water can enhance the absorption rate and capacity of CO_2 [88].

Table 3. Overview of water-based nanofluids for improvement of CO_2 absorption.

Researchers	Base Fluid	Nanoparticle	Size of Nanoparticle (nm)	Contactor Type	Enhancement %	Absorbent Loading
Arshadi et al. [111]	Water	$Fe_3O_4@SiO_2\text{-}SNH_2$	50	Bubble column	70.3	0.4 wt.%
Kim et al. [90]	Water	SiO_2	30	Bubble column	24	0.021 wt.%
Jorge et al. [128]	Water	FCNT [a]	10	Bubble column	36	4 vol%
Rahmatmand et al. [84]	Water	SiO_2	15	Batch vessel	21	0.1 wt.%
	Water	Al_2O_3	20	Batch vessel	18	0.1 wt.%
		Fe_3O_4	4		24	0.02 wt.%
		CNT	*		34	0.02 wt.%
Peyravi et al. [32]	Water	Fe_3O_4	4	HFMC	43.8	0.15 wt.%
		CNT	*		38	0.1 wt.%
		SiO_2	15		25.9	0.05 wt.%
		Al_2O_3	20		3	0.05 wt.%
Haghtalab et al. [88]	Water	SiO_2	30–40	Bubble column	7	0.1 wt.%
	Water	ZnO	11.5		14	0.1 wt.%
Salimi et al. [129]	Water	Al_2O_3	15–20	Packed column	14	0.05 vol%
		$Al_2O_3\text{-}SiO_2$	10–15		10	0.05 vol%
Salimi et al. [34]	Water	Fe_3O_4	8	Packed column	12	0.005 vol%
		NiO	50		9.5	0.01 vol%
Samadi et al. [127]	Water	Al_2O_3	25	WWC	40–55	1 vol%
Darvanjooghi et al. [93]	Water	SiO_2	62	Bubble column	40	0.01 wt.%
Ghasem [130]	Water	CNT	*	HFMC	45 [1]	0.25 wt.%
Rezakazemi et al. [131]	Water	SiO_2	15	HFMC	16	0.05 wt.%
		CNT	*		34	0.05 wt.%
Zare et al. [29]	DI Water	ZnO	10–30	PP HFMC	130	0.15 wt.%
		TiO_2	21		60	0.15 wt.%
		MWCNT	10–20		60	0.15 wt.%
Rahimi et al. [116]	Water	nMWCNT	11.6	Stirred reactor	25.1	0.02 wt.%
Devakki et al. [24]	DI Water	TiO_2	<50	Stirred cell reactor	39.81	0.1 wt.%
		Al_2O_3	<40		22.3	0.14 wt.%
Hafizi et al. [132]	Water	DETA@ECH@ Fe_3O_4	40	Batch equilibrium vessel	77.3	0.5 wt.%
Esmaeili-Faraj et al. [133]	Water	EGO	20	Bubble column	diminished to zero	<0.02 wt.%
Elhambakhsh et al. [134]	DI Water	$Fe_3O_4@SiO_2$-lysine	17–20	Bubble Column	88	0.125 wt.%
Karamian et al. [135]	Water	Al_2O_3	20–60	Single-Bubble Column	117	0.1 wt.%
		Fe_2O_3	30–80		103	1 wt.%
		SiO_2	20–60		88	0.01 wt.%
Lee et al. [136]	DI Water	Al_2O_3	45	Bubble Column	23.5	0.01 vol%
		SiO_2	15		23.5	0.01 vol%
Ansaripour et al. [137]	DI Water	α- Al_2O_3	80	HFMC	12.2	0.02 vol%
		γ- Al_2O_3	20		21.6	0.02 vol%
Golkhar et al. [31]	DI Water	CNT	*	HFMC	40	0.5 wt.%
		SiO_2	10–15		20	0.5 wt.%
Choi et al. [138]	DI Water	SiO_2	15	Stirred cell reactor	13.1	0.01 vol%

Table 3. *Cont.*

Researchers	Base Fluid	Nanoparticle	Size of Nanoparticle (nm)	Contactor Type	Enhancement %	Absorbent Loading
Elhambakhsh et al. [120]	DI Water	Fe_3O_4-proline	10–16	Stirred cell reactor	25.07	0.02 wt.%
		Fe_3O_4-lysine	13–18		31.04	0.1 wt.%
		Fe_3O_4@SiO_2-NH_2	31–39		34.23	0.1 wt.%
Manikandan et al. [95]	Water	Al_2O_3	-	WWC	19	0.6 vol%
Manikandan et al. [139]	Water	TiO_2	-	Packed column	65	1.0 vol%
		MWCNT	10	Bubble Column	36	40 Mg/L

[1]: CO_2 removal% *: Outside diameter = 8 nm, Inside diameter = 2.5 nm and Length= 10 µm. [a]: Hollow fiber membrane contactors.

Nanofluids containing different nanoparticles like SiO_2, Fe_3O_4, carbon nanotubes, or Al_2O_3 in a base fluid including amine-based solutions or deionized water were also used for gas absorption in a membrane contactor. The CO_2 absorption performance of different nanofluids from gas streams was also experimentally studied to determine the influence of different nanoparticles (Al_2O_3, SiO_2, Fe_3O_4, and CNT), in low concentrations, on the improvement of CO_2 absorption. It was revealed that unlike Al_2O_3 and SiO_2 which have better CO_2 absorption performance at high concentrations, CNT and Fe_3O_4 nanoparticles better enhance CO_2 absorption at low concentrations [84,102]. In general, when water is used as the base fluid in absorption processes, hydrophobic nanoparticles have better dispersion and a higher rate of collisions with CO_2 bubbles; consequently, the rate of CO_2 bubble cracking and as a result, the mass transfer between the two phases increases [111].

4.3. Methanol-Based Nanofluid

The methanol-based nanofluids are another kind of absorbent that improves CO_2 absorption in synthetic natural gas (SNG) systems. The high selectivity and low cost of this absorbent and the possibility of being used for high-pressure natural gas streams have made it a good candidate for these processes. Another advantage of this absorbent is the requirement of low temperatures for the regeneration process compared to the aqueous solutions since it has smaller latent heat and a lower boiling point. Therefore, the non-aqueous alkanolamines are good candidates to enhance the CO_2 absorption performance. But, according to Henry's law of solubility, it is required to keep the temperature of the absorbent at about -20 °C to be able to increase the rate of absorption [104,140]. Therefore, it needs a lot of energy to keep methanol at such a low temperature. The addition of nanoparticles to the base fluids is a perfect way of CO_2 absorption enhancement. The present research efforts are summarized in Table 4.

Table 4. Common use of methanol-based nanofluids in CO_2 absorption.

Researchers	Base Fluid	Nanoparticle	Particle Size (nm)	Contactor Type	Enhancement %	Absorbent Loading
Pineda et al. [87]	Methanol	Al_2O_3	40–50	AC, T-CA	1.2, 10	0.05 vol%
		TiO_2	<25		4.6, 5	0.05 vol%
		SiO_2	10–20		1.1, 6	0.05 vol%
Jung et al. [105]	Methanol	Al_2O_3	40–50	Bubble column	8.3	0.01 vol%
Pineda et al. [141]	Methanol	Al_2O_3	40–50	Tray column	9.4	0.05 vol%
		SiO_2	10–20		9.7	0.05 vol%
Lee et al. [104]	Methanol	Al_2O_3	40–50	Bubble column	4.5	0.01 vol%
		SiO_2	10–20		5.6	0.01 vol%
Kim et al. [78]	Methanol	Al_2O_3	40–50	Bubble column	26	0.01 vol%

Accordingly, extensive investigations were done by Jung et al., with nanofluids containing Al_2O_3 dispersed nanoparticles with 0.005–0.1 vol% concentrations. They achieved the highest CO_2 elimination of 8.3% at nanoparticle a concentration of 0.01 vol% compared to pure methanol as the absorbent. The suggested that the reason for this enhancement is the Brownian motion that induces particle-laden flows and consequently creates the mixing effects by Al_2O_3 nanoparticles [105].

Pineda et al., used a tray column to study the impact of Al_2O_3 and SiO_2 on CO_2 absorption rate when they are dispersed in a methanol-based solution. Results of their experiments showed a 9.4% and 9.7% enhancement, respectively, in the absorption capacity of nanofluids containing Al_2O_3 and SiO_2, when the optimum concentration of 0.05% of the nanoparticles was used [141]. Lee et al., also investigated the absorption performance of different methanol-based nanofluids containing different concentrations of silica and alumina particles. It was observed that the highest CO_2 absorption compared to pure methanol is achieved when 0.01 vol% Al_2O_3 or 0.01 vol% SiO_2 are dispersed in the pure methanol, in this case, 4.5% and 5.6% improvement will occur in the absorption process, respectively [104]. In another investigation, Peng et al., utilized the transient hot-wire method to determine the thermal conductivity nanofluids in which SiO_2 and Al_2O_3 are dispersed in methanol. The maximum increase in thermal conductivity was 14.29% when the nanoparticle concentration was in the range of 0.005–0.5 vol% [142]. Jung et al., utilized a bubble column to evaluate the performance of nanofluids containing Al_2O_3 dispersed in methanol-based fluids in the absorption rate of CO_2. They found that the absorption rate of the nanofluid is 8.3% higher compared to the pure base fluid [105].

In the end, different base fluids for nanofluids for the improvement of CO_2 absorption in the literature are compared in Table 5. The results indicate that the nanofluids in these fluids showed proper activity as compared with those reported in earlier studies.

Table 5. Different based nanofluids for the improvement of CO_2 absorption.

Researchers	Base Fluid	Nanoparticle	Size of Nanoparticle (nm)	Contactor Type	Enhancement %	Absorbent Loading
Devakki et al. [24]	Salt solutions	Al_2O_3	<40	Stirred cell reactor	−5.68 [1]	1 to 3.1 wt.%
		TiO_2	<50		−11.93 [1]	1 to 3.1 wt.%
Lee et al. [92]	NaCl solution	Al_2O_3	40–50	Bubble column	12.5	0.01 vol%
Nabipour et al. [89]	Sulfinol-M	Fe_3O_4	**	Quasi-static high pressure	14.7	0.02 wt.%
		MWCNT	20–30		23.2	0.02 wt.%
Zhang et al. [83]	Ammonia solutions	Fe_3O_4	20	Bubbling reactor	14.5	0.3 g/L

[1]: decreases the absorption **: Inside diameter: 5–10 nm, outside diameter: 20–30 nm and length: 10–30 µm.

5. Future Perspective

Currently, due to their positive approaches in CO_2 absorption, hybrid systems can replace common processes. Due to their novelty, on the other hand, hybrid systems require further studies to understand the effect of parameters, the performance of nanomaterials, and analysis of the process to reach an optimum rate of absorption. Some of the challenges in using hybrid systems include blockage, phase stability, lack of sufficient data in examining solvent properties, pump power, and costs of solid materials, increasing heat and energy transfer, and imposing additional investment costs. In this regard, by proper selection of nanoparticles and base liquid, two problems of energy and economy can be controlled in these systems in addition to accelerating mass transfer and increasing gas-phase absorption by solid particles. Generally, a promising perspective can be imagined in the future and at large scales by studying the relationship between mechanisms and conducting comprehensive studies on nanofluids' role in CO_2 absorption. Furthermore, CO_2 removal and absorption processes using nanoparticles and new methods will be paid more scientific attention in the future.

6. Conclusions

In this study, we have investigated hybrid systems, unique properties of nanomaterials, and their wide application in CO_2 absorption. In the last few decades, the properties of nanoparticles on a small scale with different structures have been significantly efficient in the energy field. Accordingly, we believe that such technology provides one of the effective solutions for CO_2 absorption. In this review study, in addition to the nanofluid explanation, its application, and properties using the nanofluid preparation, we have tried to address the reasons behind the base liquid selection, stability, mass transfer enhancement mechanisms in the nanofluids (shuttle effect, Bubble Breakup effect, and micro convection), and the CO_2 absorption increasing factors following the nanofluids. One of the most important points of the hybrid systems is the role of the base solvent, in which by properly selecting the nanoparticles–base solvent pair, the mass transfer rate and mechanism for CO_2 absorption have been substantially increased, accelerating the CO_2 reaction kinetics. On the contrary, lower energy consumption is required for solvent regeneration in the desorption process by decreasing the heat transfer in such systems. For this reason, in this study, the effect of 3 types of base liquid, e.g., water, amine and methanol, with different nanoparticles have been evaluated on the CO_2 absorption level. In the following, we will briefly explain the main results of this short review.

1. CO_2 absorption using nanofluids depends on several factors, i.e., particle size, nanoparticle type, temperature, and base liquid.

2. The nanoparticles preparation method and their stability are some of the important properties of nanofluids that should be taken into consideration. This is because the hybrid systems create sediments and settle over time. Accordingly, in order to control this issue, we can reform the nanoparticles' surface or the low-cost dispersions so that the stability of the nanofluids is increased.

3. The suspension preparation process is of paramount importance in terms of the type and the extent of solid particles since the nanoparticles' cost as an additive solid material to the base solvent is one of the important economic issues. Similarly, in hybrid systems, the nanoparticles synthesis is usually done using the 2-step method that is cost-effective.

4. The main mechanisms for the CO_2 absorption, the shuttle effect, bubble breakup, and the Brownian motion leading to the nanoparticles' micro convection have been thoroughly explained. It is expected that other mechanisms will be explained in this field in the future.

5. The CO_2 absorption in the nanofluid depends on the different surfaces of the nanoparticles; as a nanoparticle has a larger surface, it is dispersed better in the base liquid, increasing the absorption level.

6. There are different nanoparticles with particular applications and properties, but among them, making use of the metal oxide nanoparticles, e.g., Fe_3O_4, ZnO, Al_2O_3, TiO_2, etc., have captured significant interest in industrial applications due to being cheaper.

7. The CO_2 absorption has been investigated using three base liquids (water, amine, and methanol). Water has captured more interest among researchers as a base liquid than the two other base liquids due to availability and being cheaper.

In general, according to the research conducted in the realm of mass transfer and CO_2 absorption so far, we can conclude that using nanofluids is an effective method for increasing the CO_2 absorption in terms of the base liquid that can decrease the energy consumption and equipment costs.

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Abbreviations

AC	Annular contactor
AMP	2-Amino-2-Methyl-1-Propanol
CCS	CO_2 capture and sequestration
COPs	Covalent organic frameworks
DEA	Diethanolamine
DEPG	Dimethyl ether of polyethylene glycol
DLS	Dynamic light scattering
DW	Distilled water
EU	European Union
ESA	Electrical swing adsorption
GHG	Greenhouse gas
HFCM	Hollow fiber ceramic membrane
IIS	lonic liquids
LLE	Liquid–liquid extraction
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MOFs	Metal-organic frameworks
MWCNT	Multi-walled carbon nanotube
NGO	Nanographene oxide
NMP	N-Methyl-2-Pyrrolidone
NP	Nanoparticle
PC	Propylene carbonate
PNP	Pnitrophenol
PSA	Pressure swing adsorption
PZ	Piperazine
RES	Renewable energy sources
SNG	Synthetic natural gas
TEM	Transmission electron microscopy
TSA	Temperature swing adsorption
TVS	Temperature vacuum adsorption
VSA	Vacuum swing adsorption
WWC	Watted-wall column
Fe_3O_4@SiO_2-NH_2	Synthesiz of Fe_3O_4
Fe_3O_4-lysine	Synthesiz of Fe_3O_4
Fe_3O_4-proline	Synthesiz of Fe_3O_4

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