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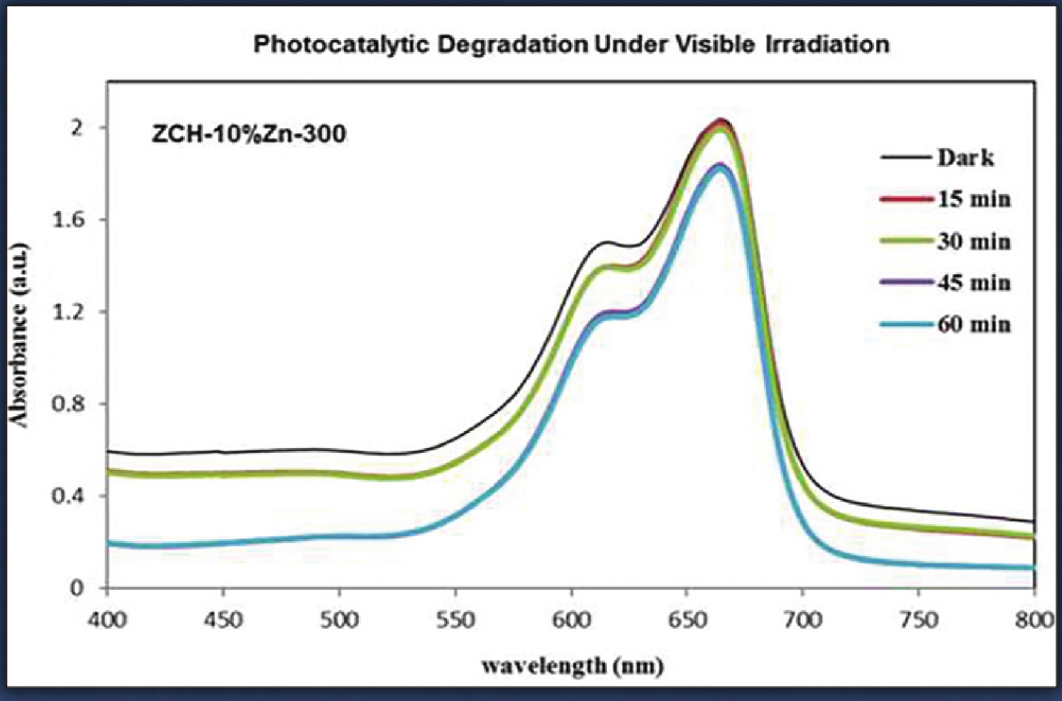

Materials and Energy Research Center

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Original Research Article

The Process of Scientometrics in the Field of Thermal Barrier Coatings as an Indicator of the Progress of Materials Engineering

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ABSTRACT

Thermal Barrier Coatings (TBCs) reduce the working temperature of the substrates and protect them from hot corrosion and oxidation. In recent years, scientific research into the TBCs and their innovative applications have gained increasing popularity insofar as since 1980, the number of relevant published articles has increased up to about 400 times annually. These coatings play an essential role in enhacing the efficiency of the substrate and engines and for this reason, tracking their research process can help advance future research studies and accelerate their progress expansion rate. According to the results from scientometrics and tracking research, the United States was initially ranked first in article production in this field of surface engineering, followed by Germany and England. However, since 2011, China has remained in the first place by a large margin. The combined annual growth rates of Iran and India reached their highest value, indicating that these countries concentrated on the gas turbine and energy sectors. Since these coatings play a significant role in improving the performance of gas turbines, variations in their scientific progress can be considered one of the leading indicators of material engineering progress in such turbines.

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1. INTRODUCTION

Thermal barrier coatings (TBCs) are refractory ceramic materials that protect the metal substrate from heat or even direct flame impact like an insulator [1-4]. These coatings are commonly used at temperatures higher than 1200 °C that can reduce the working temperature of the substrate up to 300 °C. Of note, these coatings are mainly used in air and ground gas turbines [1-8]. In terms of the coating method, these coatings can be formed by different methods such as double glazing, thermal spraying, use of vapor phase, and anodizing on the substrate [9-10]. TBCs can have different chemical compositions such as alumina, mullite, and magnesia-based composites. Generally, TBCs are zirconium materials that are stabilized with different stabilizers to

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prevent the transformation of tetragonal martensitic to cubic ZrO_2 during operation, which is caused by volume change and subsequent cracking [11,12]. The most famous of these stabilizers is Y_2O_3 [12]. An interface layer is used to improve the adhesion strength of these coatings to the substrate. This interface layer is usually MCrAlY in which M can be replaced with Fe, Co, Ni or their combination [13,14]. Another type of middle layer is aluminizing that can be reinforced by Au or Pt [15]. Another generation of these coatings is Environmental Barrier Coatings (EBCs) that work at lower temperatures as the protection against vapor and other environmental threats such as low-temperature oxidation [16,17].

The high importance of thermal barrier systems in the industry has become the incetive to carry out more research studies every year to improve these systems to the point where materials such as High Entropy Alloys and max phases have been introduced as an interface layer, and pseudo Crystals have also been considered as a new thermal barrier system or as a reinforcement of new systems [18-20]. These are just some of the developments made in surface engineering materials. Significant evolutions have also been reported in the field of Air Plasma Spray (APS) and High-Velocity Oxygen Fuel (HVOF) processes and their sub-branches [21-24]. These developments are made available annually through scientific documents such as articles or patents. Accumulation of the scientific records and documents shows the increasing attention of the academicians and industrial experts as well as the development units to these coatings. Monitoring the status of these documents to find a dynamic and constructive way to progress in TBCs is a rational solution known as scientometrics.

Scientometrics can be considered as both quantitative and qualitative analysis of the production process, distribution and use of scientific information, and factors affecting it. In addition, this science describes, explains, and predicts this process for different purposes of planning, policy-making, advancement, and Scientific-research awareness and foresight are used in individual, group, organizational, and international dimensions [25]. Scientometry is one of the most common methods for evaluating scientific activities, considering the number of scientific articles as one of the criteria for production comparison and presentation of science in different countries [25,26]. The objective scientometry pursues is to reveal the characteristics of science and scientific research by examining these variables separately or in a suitable combination. One of the most important objectives of scientometrics is to establish descriptive indicators systems in different scientific communities. The continuous and regular publication and review of such indicators can be a valuable and efficient element for research management and policy-making policies as well as allocation of budgets and facilities in science to make them more practical to meet the regional requirements [25-27]. The analysis results help determine the flow structure of the scientific documents and their citation processes. Quantitative evaluation of sciences leads to development while assisting the officials and planners in making the most of financial and human resources at lower costs and being effective in optimizing the economic-social structure of a country. In addition to looking for the quantitative aspects of science and research, scientometry also measures and determines the standards of various managerial and organizational aspects of science. On a broader level, scientometrics can be considered one of the influential factors in the continuous circulation of research activities in any scientific field, which directly deals with the quantitative evaluation of science [27,28].

This report analyzes research papers written about TBC from 1980 to the end of 2021 using Scopus data. In this regard, the findings were analyzed to monitor the progress of TBCs and identify the leading countries in this field. In addition, the country which has made significant strides in this field was identified, thus making it possible to predict the trend of future changes and determine the policy of research in this field.

2. MATERIALS AND METHODS

Articles on TBC written from 1980 to 2021 in Scopus with the keywords "(TITLE-ABS-KEY ("thermal barrier" OR "thermal barriers") AND TITLE-ABS-KEY (coating OR coated OR coatings OR coat)) OR TITLE-ABS-KEY (thermal AND TBC))" were searched and found. A total number of 11253 articles were published, and the information of the articles such as their authors, publication year, title, reference title, abstract, organizations and affiliation, keywords, and other related data were prepared as a Commonly Separated Value (CSV) file. Next, the obtained data were processed and analyzed using VOSviewer software. The extracted graphs were analyzed using a detailed study of relevant sources and articles in the field of TBC.

3. RESULTS AND DISCUSSION

Figure 1 shows the results obtained from the number of publications published in different years (the mentioned period). According to this figure, this topic has clearly gained in increasing significance every year, as evident from the increasing trend in the number of articles as time went by.

Since 1997, more attention has been paid to this type of coating due to the greater demands for energy and transportation. The increasing trend has been maintained in all years until 2017 and 2018, when around 700 valid scientific documents were published annually. This shows the importance of these coatings in various industries such as gas turbines, power plants,

petrochemical industries, aerospace, military, defense, and transportation. On the contrary, considerable attention to surface engineering sciences in recent years shows the need for the temperature rise in many industries since an increase in temperature leads to the higher efficiency of the internal combustion engines [29]. Therefore, more research in this field is required to improve productivity in industries.

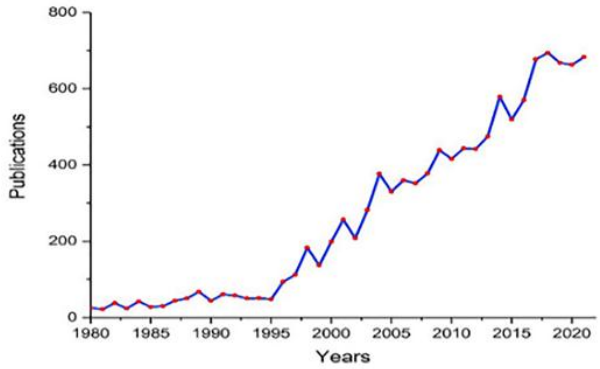
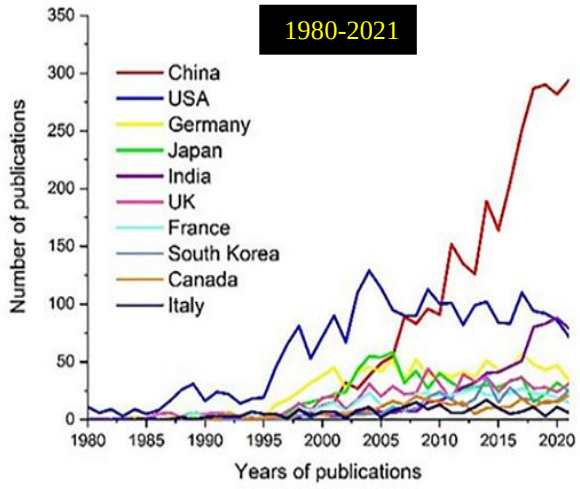


Figure 1. The number of articles published about TBC in different years

Figure 2 shows the number of published articles in 10 leading countries in the field of TBCs. Followed by separating the articles produced according to country, it can be concluded China with about 3000 publications is the leader in this field. Other countries such as the United States, Germany, Japan, and India are in the next positions, showing that these countries are either active in producing the raw materials of these coatings or are developing the technology for applying these coatings, both of which indicate the attention of these countries to the TBCs and their development. However, due to the importance of industries in their country, these countries pay special attention to the mentioned coatings.



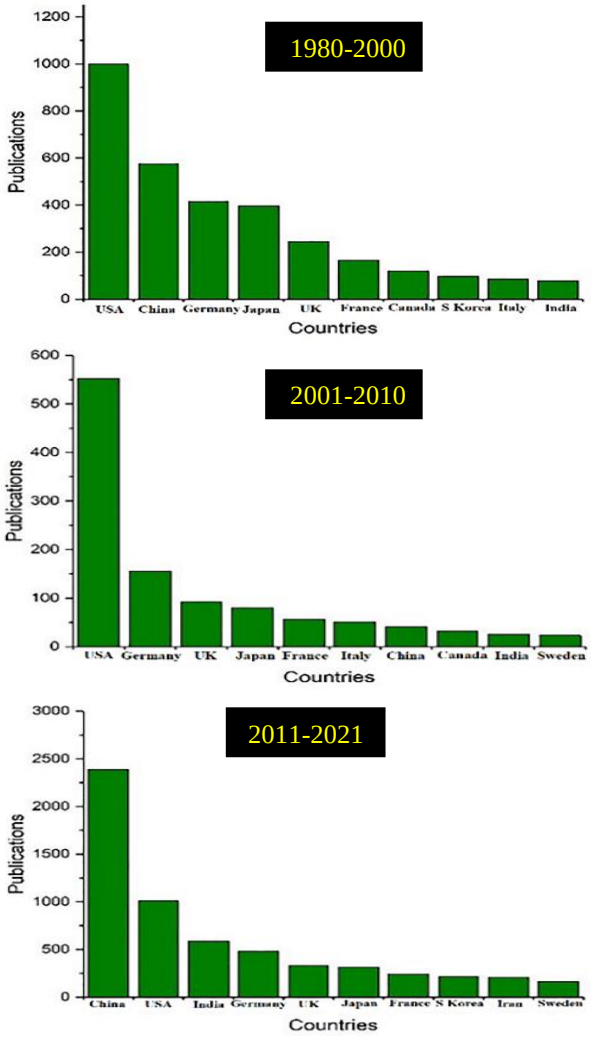


Figure 2. The number of resources produced about TBC in different countries

The United States used to be the leader of scientific production in this field until 2010; however since 2011, China has overtaken the United States' place and moved from seventh place in the years before 2000 to the first place. Iran did not have any articles on the discussed subject until 2000 but after 2001, it had acceptable growth until it reached the ninth rank in 2011.

As observed in Figure 2, between 1980 and 2000, a majority of the articles were published in the United States of America, followed by China and Germany. From 2001 to 2010, China occupied the second place, and Germany and Japan maintained their upward trend and took the third and fourth places, respectively. However, between 2011 and 2021, China, the United States, and India were in the top three countries producing science and have been active in this scientific field of surface engineering, indicating the great attention of these countries to the energy field and increasing productivity in the last decade. England and Japan are

other active countries in this field. Iran has also reached the top ten science-producing countries in this field in the last decade, indicating the sustainable development and training of excellent experts in this field.

In order to properly examine the growth rate of the number of articles in each country, an index called Compound Annual Growth Rate (CAGR) [30] is used, the results of which are shown in Figure 3. The years 2000 and 2010 were selected as the time origin, and the present time is chosen as the end of the analysis period.

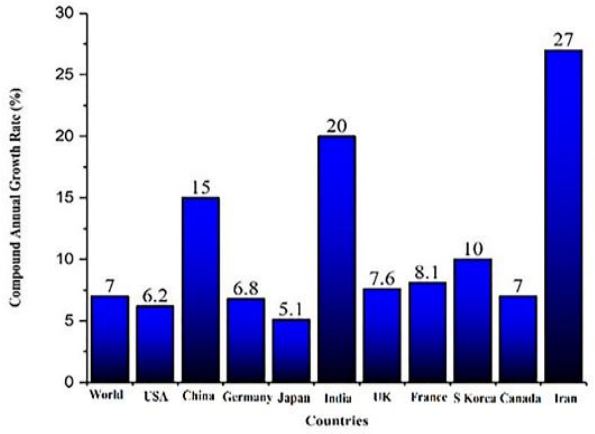


Figure 3. The compound annual growth rate of the ten most active countries in TBCs from 2000 to 2021

According to the observations, the United States has published a high number of articles; However, compared to the past, the process of producing articles in America in this field has slowed down. Between 2001 and 2010, the number of articles was under 200 while between 2011 and 2021, this number increased up to nearly 1000. However, other countries such as India, China, and Iran showed a high annual growth rate. In this regard, Iran can be considered a leading country producing many articles in a short period of time followed by India and China. This shows Iran's progress in gas turbines and related sciences. Publishing articles about the gas turbines, such as TBCs, shows the country's attention to industries related to gas turbines, such as aerospace, gas transmission, and power plants. Paying attention and spending time on scientific projects in the field of gas turbines shows both considerable interest to and a measure of progress in that field, thus promising the efficiency of these industries.

As mentioned earlier, to rank the leading countries and their connections with each other in the field of TBC research, Scopus database data and VOSviewer software were used. Among the 212 active countries in this field, only 33 have authored more than 30 titles. The relationship between these countries is shown in Figure 4.

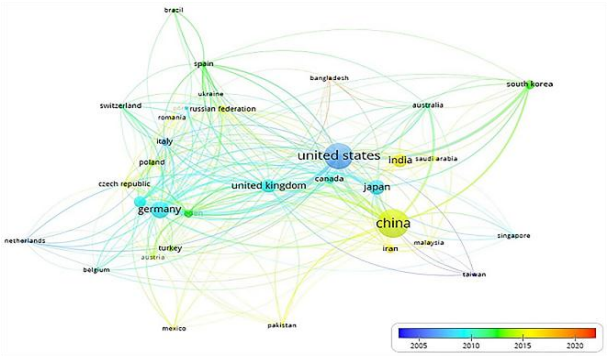


Figure 4. The map of the countries that are active in the field of TBC and their research cooperation with each other

The circle size of each country shows the number of publications relatively while the thickness of the communication lines indicates the strength of communication between countries. The color changes indicate the annual average of the article publications which at the end, shows the distance between the two countries and the proximity of the researchers of the two countries. The United States and China are the leading countries while other countries such as Germany, Japan, and England have either started their activities in recent years or have reduced the amount of their research over time.

While checking the communication network among the keywords in articles about thermal barrier coating, 37739 unique words were found only 28 of them from this collection were repeated at least 500 times. Then, the following result was obtained (similar words were removed). In Figure 5, the size of the circles is indicative of the repetition of the words as well as the lines of connection between the two words. The colors also indicate the year. According to the subject under study, the words Plasma Spraying, Thermal Barrier Coating, and Coatings have been repeated numerously. As a result, these words have a larger circle than the rest. Among the types of coatings, Zirconia, Yttria Stabilized Zirconia, and Alumina have been more critical, showing that these coatings with the Plasma Spray method are the most used in industry and research works.

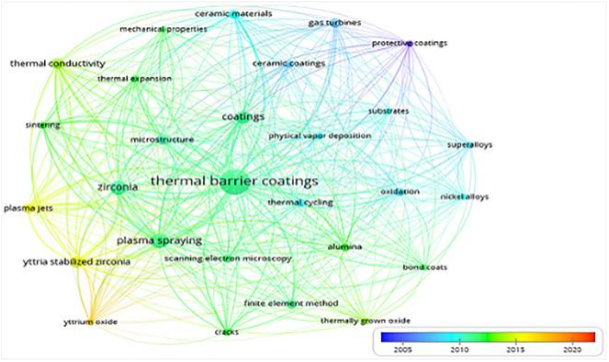
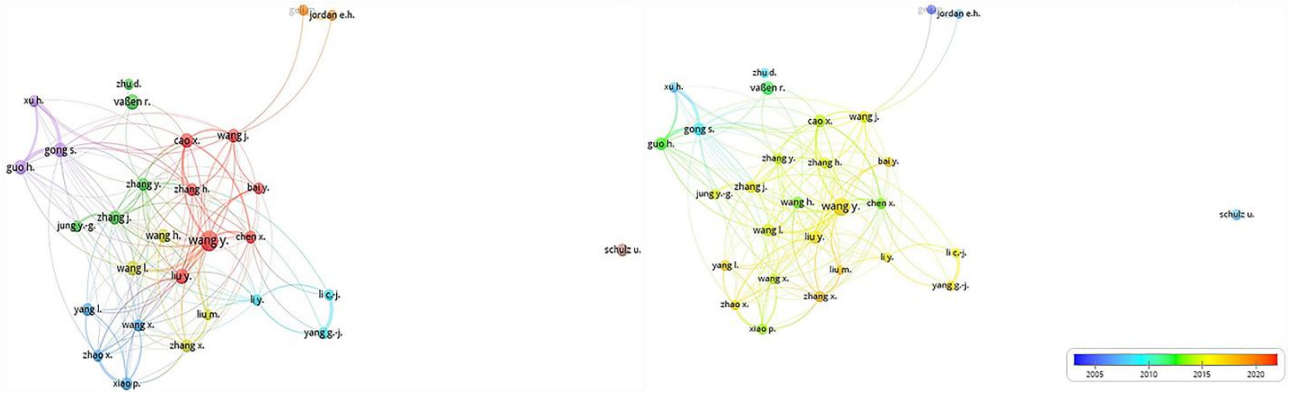


Figure 5. Network of frequently used words in TBC

The network between researchers is drawn in Figure 6(a) with more than 70 titles of authorship based on the research groups (each color represents the relationship of people with each other), and Figure 6(b) is drawn based on the publication year. Out of 16899 authors, 29 researchers have authored more than 70 titles. The most communication network with 19 researchers is related to a researcher named Amy Wang. Some centers and universities that are active in the field of thermal barrier coating are shown in Figure 7. As observed, some centers such as NASA, the German Air Force, and the Oak Ridge National Laboratory were active before 2000. However, academic and research centers and academic centers have taken over most scientific production in this field since 2016.



(a) **(b)**

Figure 6. The communication network of researchers according to the (a) research groups and (b) publication year

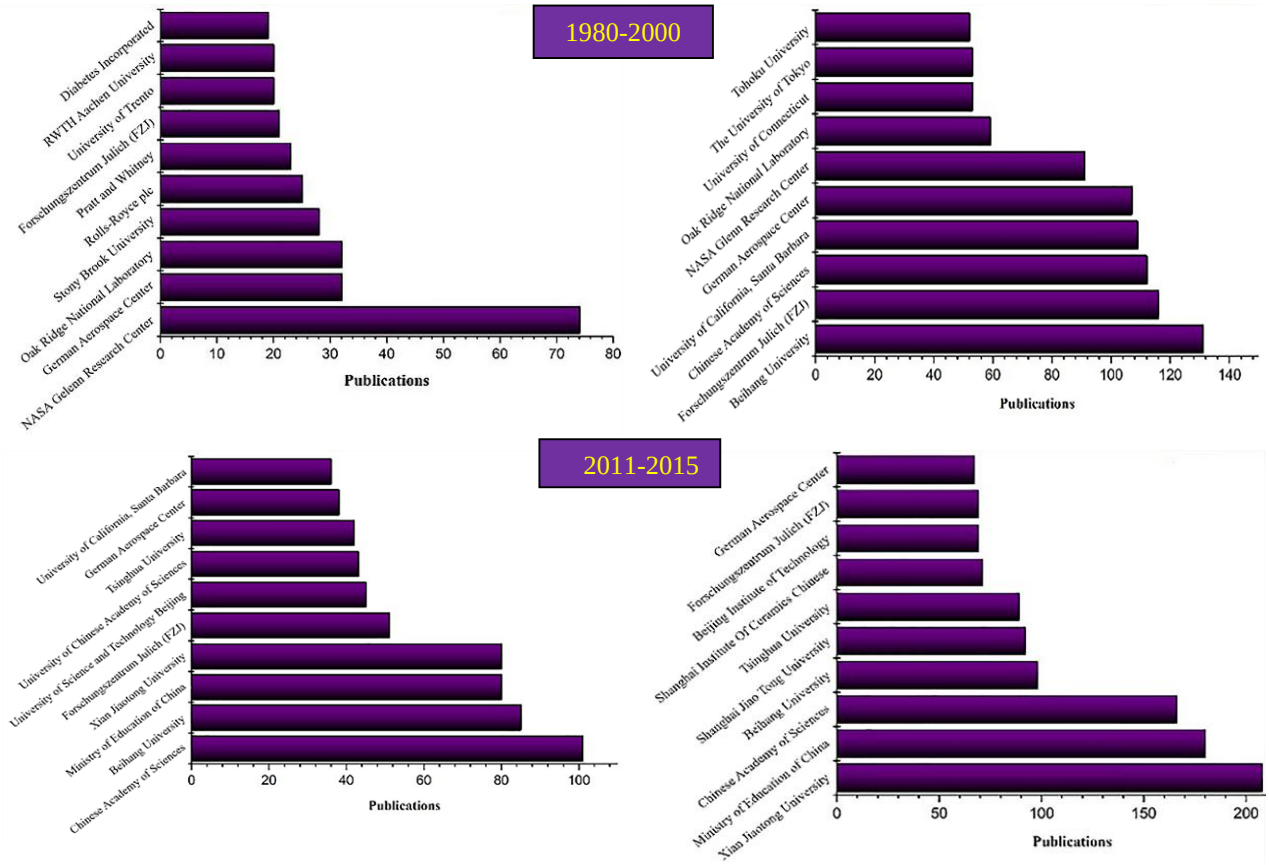


Figure 7. Active centers that conduct research in thermal barrier coatings in different time frames

4. CONCLUSIONS

The following results can be obtained from the current research:

1. In recent years, TBCs have drawn considerable attention which is more tangible in developing countries than the developed ones.
2. In the beginning, the science production rate in TBCs was high in the United States, Germany, and England, and this growth was at the highest level in China, the United States, and India.
3. China has gained the highest number of articles by publishing numerous articles and has reached the top position with a stable trend. Iran has also the highest position in compound annual growth rate. This issue shows the attention of these two countries to TBCs.
4. However, compared the past, the process of producing articles in America in this field has slowed down. Between 2001 and 2010, the number of articles was under 200 titles while between 2011 and 2021, their number increased up to nearly 1,000.
5. Publishing articles in the fields related to gas turbines, such as TBCs, shows the increasing attention of these countries to the industries related to gas turbines such as aerospace, gas transmission, and power plants. Paying attention and spending time on scientific projects in the field of gas turbines shows the considerable attention and a measure of progress in that field, which can also be found in the efficiency of these industries.

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Original Research Article

In Vitro Evaluation of Manganese-Containing Glass-Ceramic in Quaternary SiO_2-CaO-Na_2O-P_2O_5 System

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ABSTRACT

In this research, sol-gel experimental conditions are imposed to prepare a new Mn-containing SiO_2-based bioactive glass. The current study primarily aims to investigate the impact of the presence of manganese ion on the glass structure, bioactivity, and cytotoxicity. The obtained glass-ceramics were characterized using a X-Ray Diffractometer (XRD). According to the observations, crystallization of silicorhenanite and calcite phases in the manganese-containing sample were inhibited before and after soaking in the simulated body fluid (SBF), respectively. In vivo bioactivity evaluation confirmed the bioactive nature of the obtained powders. Finally, the cellular test was carried out, the results of which demonstrated non-cytotoxicity of the samples towards human Bone Marrow Stromal Cells (hBMSCs) cells up to 7 days.

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1. INTRODUCTION

The term biomaterial refers to man-made materials used for repairing or restoring body functions after they have been injured or damaged. To be effective as bone tissue replacement, a biomaterial must be non-toxic with the ability to form a hydroxyapatite (HA) layer on its surface to decrease the rejection potential [1]. Generally, biomaterials can be divided into three groups: bioinerts (non-toxic and biologically inactive), bioactives (both nontoxic and biologically active), and biodegradables or bioresorbables (dissolved and replaced by the surrounding tissues, called the third-generation materials) [1,2]. Bioactive glasses (BGs) are nontoxic biomaterials that exhibit bioactivity in orthopedics through their interactions with body fluids [3-5].

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Recently, application of biologically active ions has gained more significance than ever to enhance the biological and physical effectiveness of BGs and develop multifunctional biomaterials with a wide range of biomedical applications [6-8]. In addition to their essential role in human health, metallic ions can be a cost-effective alternative to pharmaceuticals [9-11]. Incorporation of metallic ions into BGs has been extensively studied in recent years [7,10,12-14]. Manganese plays a critical role in both bone and muscle metabolism [15,16]. Manganese present in the human body help prevent bone loss caused by free radicals and therefore, its prolonged deficiency can cause osteoporosis. Low manganese levels can be detected in osteoporotic patients [10,17]. Luthen et al. [18] investigated the effects of different manganese ion on the cellular functions like spreading, proliferation as well as gene expression in human osteoblasts by directly introducing different concentrations of $MnCl_2$ to the cell suspension (0.01–0.5 mM). Their result showed a strongly concentration-dependent effect of manganese cations on the cell functions, which should be adjusted through incorporation to different biomaterial. Manganese-containing bioactive glasses have also been investigated in recent years [12,16,19-25]. Compared to Mn-free glasses, those glasses that contain manganese in their composition enjoy an increase in the osteoblast differentiation, bone mineralization, Alkaline Phosphatase (ALP), and bone morphogenetic protein expression [16]. It was found that Mn-doped samples exhibited significant bioactivity, given the formation of HA after only a few hours and their complete coverage after fourteen days [25]. Further, the antibacterial properties of these glasses were identified [26]. The research findings confirmed that 1.6 ppm of Mn^{2+} in basal Dulbecco's Modified Eagle Medium (DMEM) stimulated the osteoblast proliferation without impairing cell viability [23]. Based on these studies, Mn incorporation into the bioactive glass networks can provide superior bone regeneration materials. However, in most studies, the presence of alkaline or alkaline earth elements has been completely neglected or small amount of these ions have been investigated. Considering the advantages of these elements, the current study aimed to synthesize and evaluate the bioactive glass containing significant amounts of alkaline and alkaline earth ions along with manganese ion, which can be considered an innovation in academic milieu. This research aimed to produce a sol-gel manganese-containing SiO_2-based bioactive glass with high alkali and alkaline earth oxide content ($52SiO_2.(30\text{-}x)CaO.14Na_2O.4P_2O_5.xMnO$, x = 2 (mol %)) to obtain a potential biomaterial for bone tissue regeneration. In addition, it evaluated the effect of Mn incorporation on the sample structure, cytotoxicity, and in-vitro bioactivity.

2. MATERIALS AND METHODS

2.1. Bioactive Glass Powder Synthesis

All chemicals used in this study were purchased from Merck and Sigma-Aldrich and used as received. Calcium-nitrate-tetrahydrate ($Ca(NO_3)_2.4H_2O$), manganese nitrate-tetrahydrate ($Mn(NO_3)_2.4H_2O$), sodium nitrate ($NaNO_3$), tetraethyl-orthosilicate alkoxides (TEOS, $Si(OC_4H_9)_4$), and triethyl phosphate (TEP, $P(C_2H_5O)$) were used as precursors. Deionized water and absolute ethanol were used as solvents, and 0.05 M citric acid was used as the sol-gel reaction catalyst. The sol-gel process was used to prepare Mn-free and Mn-containing glass powders as discussed in our previous work [27]. First, TEOS and TEP were diluted in ethanol and then, $NaNO_3$ and ($Ca(NO_3)_2.4H_2O$) were dissolved in an acidic solution, respectively. In the next step, the former solution was gradually added to the latter. The resultant solution was stirred for three hours until complete hydrolysis was achieved. Next, the solution was sealed and left at room temperature for gel formation. The obtained gel was aged at 70 °C for 24 h and dried at 110 °C in an oven for 24 h. Finally, the dried sample was calcined at 650 °C for an hour (3 °C/min). To obtain Mn-containing glass (2Mn-BG), Mn was introduced into the glass by partial replacement of the calcium content. For this purpose, a similar process to BG synthesis was applied except that ($Mn(NO_3)_2.4H_2O$) was added to the acidic solution before ($Ca(NO_3)_2.4H_2O$) dissolution.

2.2. Powder Characterization

The as-prepared products were analyzed using X-Ray Diffraction (XRD, DRON-8, Bourevestink, Russia, CuKα, 40 Kv, λ = 1.5418 Å). Scanning was carried out from 15 to 100° with a step size of 0.026° per step at step time of 49.2 s.

2.3. In Vitro Bioactivity Assessment

The bioactivity of the synthesized powders was evaluated by immersing them in Simulated Body Fluid (SBF), according to the approved Kokubo protocol [28]. For this purpose, 15 mg of glass powders were immersed in 15 ml of SBF in polyethylene bottles and kept in an incubator (Memmert GmbH-CokG, Germany) at 37 °C for 14 days. The initial pH of SBF was kept at 7.4. The HA layer formation was confirmed by the EDX and XRD analyses after 14 days of immersion in the SBF. At each time, the point samples were removed from SBF, rinsed with distilled water, and dried in an oven at 60 °C. To study the dissolution process of the synthesized powders, the pH variation of the samples was also recorded. The pH variations for the SBF-soaked sample were measured at the intervals of 1, 3, 7, and 14 days by an electronic pH meter (BEL, PHS3-BW, Italy).

2.4. Biological Tests

2.4.1. Cytotoxicity

Cell viability was investigated by conducting MTS (3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium) assay, a calorimetric method for quantification of tetrazolium compounds reduction into a water-soluble purple formazan by viable cell mitochondria. The indirect assay was then carried out following the 10993-5 States [29]. The ionic products of the samples were obtained as follows: the powder samples (BG, 2Mn-BG) were first sterilized by UV radiation for an hour and then, the samples were suspended in basal DMEM culture medium at the concentration of 1 mg/ml for 24 h at 37 °C. To obtain a better understanding of cell viability, the cells were treated with different concentrations of powders for prolonged periods. Consequently, the extracts were diluted using DMEM to achieve 1000, 100, and 10 µg/mL final concentrations and filtered (0.22 µ), and the test was carried out at different time points (1, 3, and 7 days). Meanwhile, human Bone Marrow Stromal Cells (hBMSCs) were seeded in a 96-well plate containing 200 µl DMEM supplemented with 15 % FBS and 1 % antibiotic with the density of 5 × 103 cells/well. The cultured cells were incubated at 37 °C with 5 % CO_2 for 24 h. Subsequently, the cell culture media were removed and replaced by the extracted media and incubated for 1, 3, and 7 days. During 1 and 3 days, the powders suspension added at the beginning was used and after 5 days, the culture media was replaced by the new aliquots of extracts. The cells grown without sample extracts were next used as control. At the predetermined time, the extracts were removed and replaced with the 80 µl fresh medium and 20 µl of MTS solution (2 mg/ml). These cells were incubated for 3-4 h at 37 °C in a humidified atmosphere of 5 % CO_2. Finally, the absorption was determined using a spectrophotometer (Synergy HT, BioTek, U.S.A.) at 490 nm wavelength. The cell viability is determined using Equation (1):

$$\% \text{ Cell viability} = \frac{\text{Mean absorbance of samples}}{\text{Mean absorbance of control}} \times 100 \quad (1)$$

All materials used in the cell culture process were obtained from the Gibco brand (Thermo Fisher Scientific, USA).

2.4.2. Statistical Analysis

All experiments were conducted in triplicate and presented in means ± Standard Deviation (SD). Statistical differences of these values were evaluated using one-way Analysis of Variance (ANOVA) using prism software. Here, $P < 0.05$ was considered statistically significant.

3. RESULTS AND DISCUSSION

3.1. Phase Analysis

Figure 1 shows the diffraction patterns of the synthesized powders stabilized at 650 °C for one hour at the heating rate of 3 °C/min. The BG diffraction pattern confirms the presence of combeite $Na_2Ca_2Si_3O_9$ (PDF#075-1687) and pseudo-apatite crystalline phase of silicorhenanite $Na_2Ca_4(PO_4)_2SiO_4$ (PDF#032-1053) without any traces of nitrate phases related to the used precursors. Apparently, the synthesized powders are glass-ceramic. Addition of manganese oxide caused a change in the powder color from white to light brown. A comparison of the diffraction patterns of BG and 2Mn-BG powder confirmed the diminishing of the peaks attributed to the silicorhenanite phase. Therefore, it can be concluded that the presence of manganese prevented the crystallization of this phase. Calcium content in the 52S4 glass, combeite, and silicorhenanite phase is approximately 21, 23, and 33 wt. %, respectively. It should be noted that formation of the silicorhenanite crystalline phase requires a higher calcium content. In this respect, that silicorhenanite formation was hindered by addition of Mn instead of CaO is acceptable. The results from evaluating the effect of manganese on the structure of 45S5 glass-ceramic confirmed that the presence of manganese caused a decrease in the degree of powder crystallinity [30]. In addition, amorphous phases proved to show higher bioactivity than the crystallized samples with the same composition [31].

The XRD results revealed that the presence of MnO could not guarantee the formation of any new phase, and no peak attributed to the primary manganese precursor was observed in the diffraction pattern, indicating that Mn^{2+} was embedded in the glass-ceramic structure.

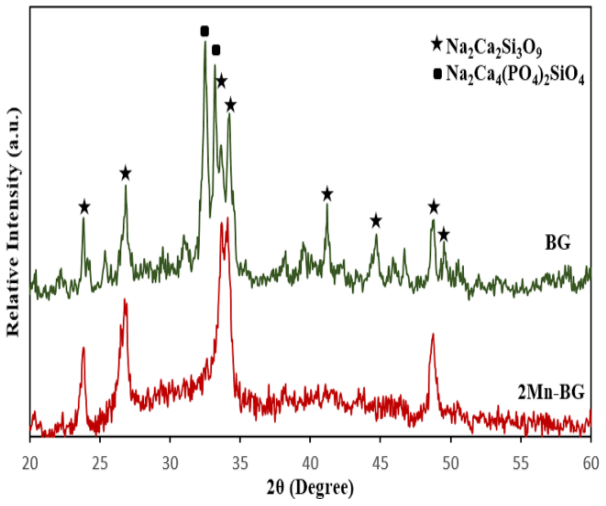


Figure 1. XRD patterns of BG and 2Mn-BG powders stabilized at 650 °C for 1 h with a heating rate of 3° C/min

3.2. In Vitro Bioactivity

The in vitro HA layer formation on a material surface is indicative of the in-vivo bioactivity of the material [4,32]. The formation of the HA phase requires the ionic interaction of biomaterial and SBF; therefore, different factors including the material composition and its degradation rate affect the thermodynamics and kinetics of the reactions [33].

Figure 2 shows the pH variations during the SBF soaking for BG and 2Mn-BG. As observed, the pH values increased in the first three days of immersion and then up to day 7, these values decreased until they finally reach a rather constant value up to day 14. The pH variations in the SBF result from the exchange of ions between the SBF and the samples. As accepted, after the glass-ceramic immersion in the SBF, alkaline, and alkaline earth ions, like Na^+ and Ca^{2+}, enter the SBF and react with the hydroxyl groups forming bases that increase the pH, such as $Ca(OH)_2$ and NaOH. In the next step, Ca^{2+} ions are adsorbed onto the surface (CaO-P_2O_5-rich layer precipitation) and once again, the pH value is reduced. The constant pH values at longer times indicate a balance between these two processes, namely ion release into the solution from the material surface along with reabsorption of these ions from SBF and precipitation of CaO-P_2O_5-rich layer on the surface [16,34]. The above-mentioned trend was detected for both samples, and no significant difference in the pH values was observed for the BG and 2Mn-BG samples while being soaked in the SBF environment.

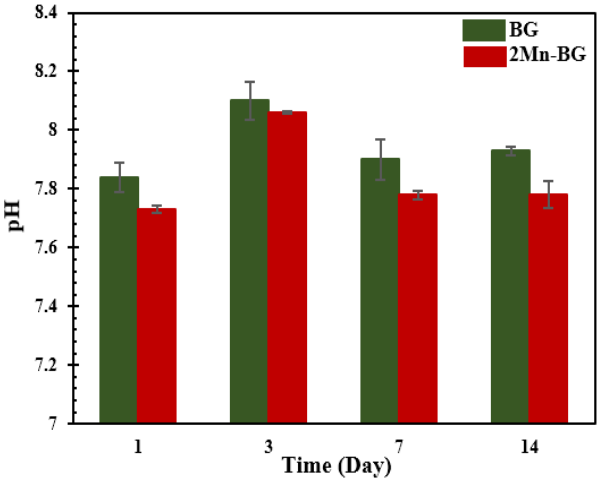


Figure 2. The pH value in the synthesized powders up to 14 days immersion in SBF

Table 1 shows the elemental analysis of the powders before and after in vitro test in SBF after 14 days. A decrease in the Ca and an increase in the Si content were observed on the surface of both samples, thus confirming the release of Ca^{2+} ions into the SBF and formation of a silicon-rich layer on the surface of samples.

TABLE 1. Ion concentration of synthesized powders according to EDS analysis before and after immersion in SBF

Elements	BG		2Mn-BG	
	Before soaking (wt. %)	After soaking (wt. %)	Before soaking (wt. %)	After soaking (wt. %)
Si	13.27	28.32	13.90	21.31
Ca	20.29	13.15	16.56	7.49
Na	11.74	0.13	12.76	2.52
P	0.73	3.01	0.97	1.60
Mn	-	-	3.5	2.95

Figure 3 shows the XRD pattern of the samples after immersion in the SBF. The patterns confirm the formation of HA phase ($Ca_{10}(PO_4)_6(OH)_2$; PDF#09-0432) with the main peak at around 32 degrees in both samples, confirming the bioactive nature of the powders.

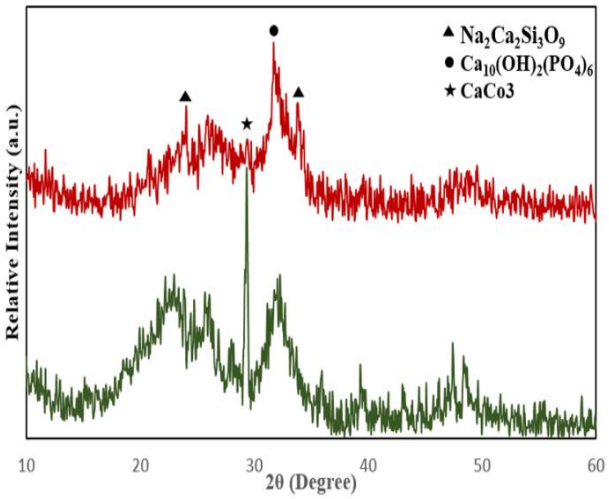


Figure 3. XRD patterns of the BG and 2Mn-BG samples after 14 days of immersion in SBF

The major peak for calcite at about 29° ($CaCO_3$; PDF#00-001-837) appeared in the BG diffraction pattern after immersion. This peak, however, almost disappeared in the diffraction pattern of the manganese-containing sample. The reaction between the high contents of Ca^{2+} and $(CO_3)^{2-}$ ions, released from glass powder particles and SBF solution, respectively, was the main reason for calcite phase precipitation [35-37].

The higher amounts of calcium oxide in the Mn-free sample could be the reason for calcite precipitation [38,39].

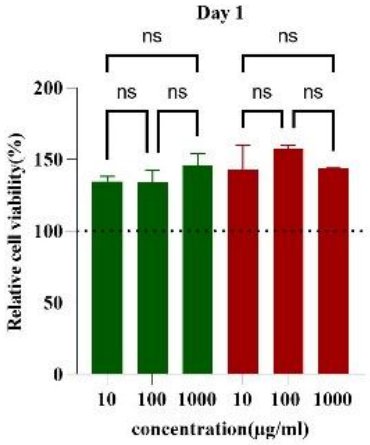
In addition, the presence of Mn in the glass would enhance its durability by creating stronger Mn–O–Si bonds than those created by Ca–O–Si [35,30]. The stronger bonds in turn reduce the Ca release rate into the

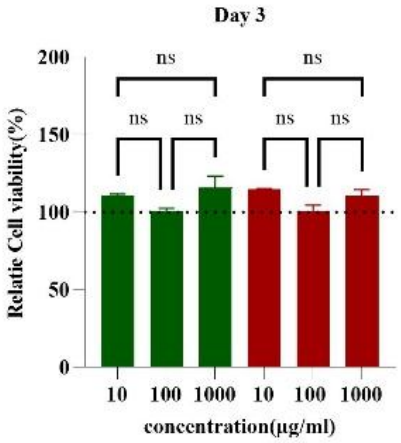
SBF and inhibit calcite precipitation. The peaks related to the combeite phase can be observed in the 2Mn-BG powders pattern. Based on the obtained results, it can be concluded that the presence of manganese stopputs an end in the ped calcite deposition without any negative effect on bioactivity.

3.3. Cytotoxicity Evaluation

The cytotoxicity was evaluated by hBMSCs exposure to the ionic dissolution of the synthesized powders. As indicated in Figure 4, no cytotoxic effect was observed with the dissolution products of the prepared samples at three different concentrations of 1000, 100, and 10 µg/ml. Of note, an increase in the cell proliferation was observed in the hBMSCs exposed to the conditioned media for up to seven days at higher concentrations.

It can be concluded that the dissolution products of the synthesized powders can enhance the proliferation potential of cells and produce higher levels of cell function, compared to the control group, meaning that Mn-containing samples are not cytotoxic under the evaluated conditions.





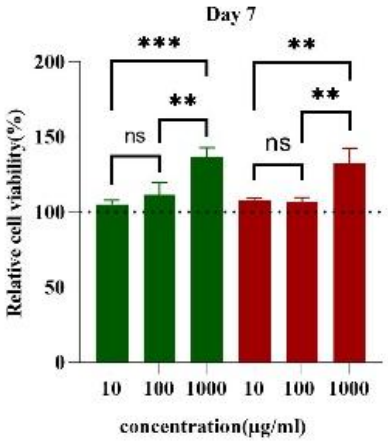


Figure 4. Viability of hBMSCs in the presence of increasing concentrations of synthesized powders (10, 100, and 1000 µg/ml). Green: BG, Red: 2Mn-BG. Data presented as mean ± SD of three independent sample, n=3. (ns indicates not significant differences, ** indicates $p < 0.05$, and *** indicates $p < 0.02$)

4. CONCLUSION

In this study, manganese-free and manganese-containing glass-ceramic in the quaternary system SiO_2–CaO–Na_2O–P_2O_5 were synthesized using the sol-gel route. The results indicated that combeite and silicorhenanite were crystallized in the Mn-free sample followed by heat treatment at 650 °C for one hour. However, the Mn ion addition inhibited the crystallization of the silicorhenanite phase. The in-vivo bioactivity test on both BG and 2Mn-BG samples confirmed their noticeable bioactivity. Further, calcite precipitation was diminished in the 2Mn-BG sample. The MTS test results demonstrated the nontoxicity of BG and 2Mn-BG samples towards the hBMSCs cells such that an improvement in the mitochondrial activity of these cells was observed until 7 days.

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Review Article

Composition, Properties, and Standards for Cementitious Ceramic Tile Adhesive: A Review

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ABSTRACT

The simplicity and widespread use of adhesive mortars for affixing ceramic tiles as ornamental finishes for indoor and outdoor applications has flourished the market of adhesive dry mortars. In tilling technology, attaching ceramic tiles to different types of surfaces requires a mortar with the requisite workability, flexibility, and adherence. With the evolution of building industry, mortars are now manufactured as ready-to-use products in which mineral binders and aggregates are properly combined. In addition to the fundamental components (cement, lime, sand), additional additives and admixtures are frequently added to the mortar formulations to improve their specifications and achieve varied technical features. Depending on their application purposes, incorporation of these additives and admixtures should be examined in depth to obtain the most significant contributions. In this regard, this article examines the already conducted studies and research works concerning Cementitious Tile Adhesives (CTAs) and explores the adhesion mechanisms, CTA constituents, classification, and standards, and performance evaluation of the cementitious ceramic adhesive. The results from extensive research indicate that a number of distinct parameters affect the adhesion properties of the CTAs. However, further studies are still required to enhance their engineering attributes.

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1. INTRODUCTION

Adhesive is a substance applied to one or more surfaces of two different components, which permanently binds them together and prevents their separation [1]. Based on the adhesion process, adhesives are often categorized into two types of reactive and non-reactive.

Likewise, they can be divided based on their ingredients, chemical composition, mechanical properties, or physical phase. According to the building application, adhesive materials are categorized as follows:

- Cementitious adhesives
- Paste or ready-to-use adhesives
- Organic adhesives

2. ADHESION MECHANISMS

Several interdependent mechanical, physical, and chemical forces are involved to bond an adhesive to a substrate. The five adhesion mechanisms are mechanical,

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electrostatic, physical absorption, chemical absorption, and diffusion, and it is impossible to isolate these forces from one another [2,3].

2.1. Physical Adhesion

This type of adhesion is the result of molecular contact between two materials that are bonded by van der Waals forces. Figure 1 shows a schematic of this adhesion and the force that causes it. Van der Waals force is the weakest force in the adhesive connection but it is reasonably sufficient enough to make strong connections [4].

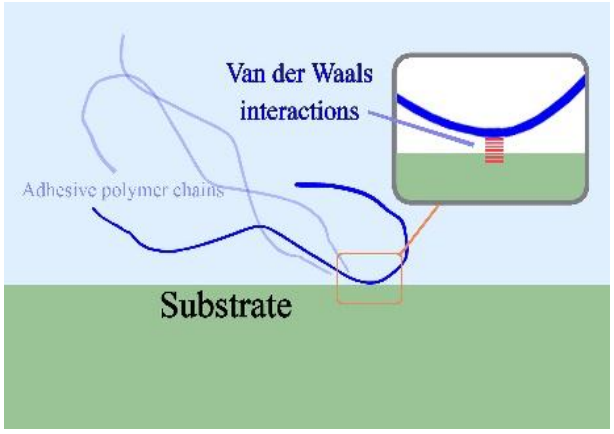

Figure 1. A schematic of surface forces in physical adhesion

2.2. Chemical Adhesion

Chemical adhesion is referred to as the formation of ionic, covalent, or hydrogen bonds at the interface of two components. Two substances are connected by either exchanging electrons (ionic bond) or absorbing hydrogen, oxygen or fluorine atoms to a hydrogen atom (hydrogen bond). Chemical bonds are strong and significantly contribute to the adhesion of two components. Figure 2 shows the schematic of this type of connection.

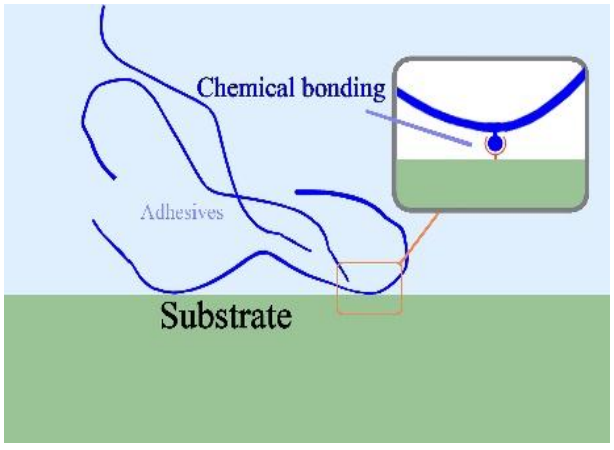

Figure 2. Schematic of the chemical connection between the adhesive and substrate

2.3. Diffusion Adhesion

Adhesion of polymer materials results from the interpenetration of chains at the interface. This type of adhesion is created when both the adhesive and substrate are polymers and when they can dissolve in one another. The interface between an adhesive and a substrate before and after diffusion bonding is depicted in Figure 3. Atoms diffuse from one component to another when a polymer adhesive and substrate are contacted with one another and heated, which results in adhesion. Temperature, contact time, polymer molecular weight, and physical state (liquid or solid) all affect the diffusion adhesion [4].

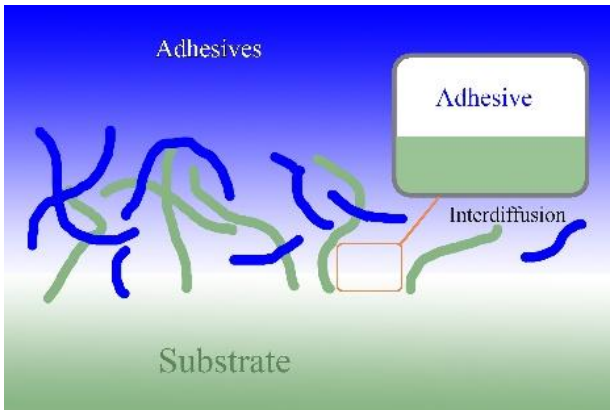

Figure 3. Schematic of diffusion adhesion between the adhesive and the substrate

2.4. Electrostatic Adhesion

The theory of electrostatic adhesion refers to the difference in electric charge at the interface between two materials where the electrons are transferred from one material to another. This phenomenon creates an attractive force between these materials which facilitates adhesion. An electrical double layer is depicted in Figure 4 as a result of an adhesive adhering to a substrate. This theory will not be applicable if one or both of the connected materials are insulators [4].

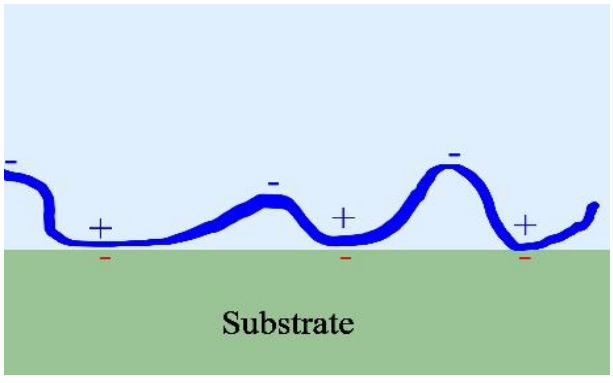

Figure 4. Negative and positive electric charges in the connection of materials

2.5. Mechanical Adhesion

According to the principle of mechanical bonding of the adhesives, a proper adhesion can occur only when an adhesive interlocks holes pores, cracks, and other surface roughness of the substrate, and it is mechanically locked to the substrate. Figure 5 illustrates how surfaces have always some degrees of roughness, hence never fully smooth.

To be specific, an adhesive should move the trapped air at the interface, interlock the surface pores, and provide a mechanical lock with the interface. It also implies that the adhesive must possess the necessary rheological characteristics to fill the gaps in a timely manner in addition to wetting the surface [4].

The surface roughness helps the adhesion force to create a larger contact surface. The total surface contact energy rises as a result of this issue, thus increasing the resistance to separation. Of note, the adhesive must wet the substrate to form a strong bind.

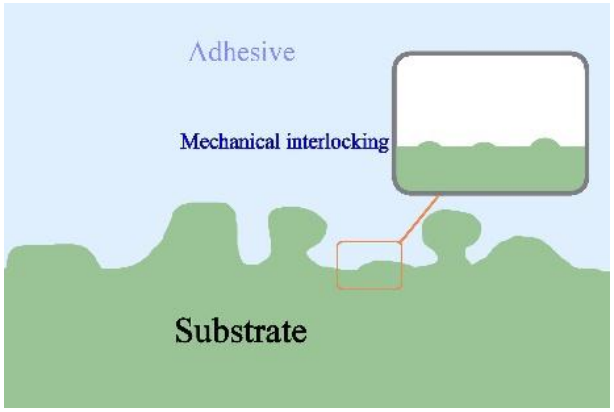

Figure 5. Mechanical locking between the adhesive and the substrate

3. THE HISTORY AND APPLICATION OF DRY MIX MORTARS

The usage of mortars has a long history, dating back to the time when the mineral mortars were widely utilized in building and architectural constructions. Roman construction refers to a state where the cement paste, i.e., a mortar (lime and sand or pozzolan) mixture, was first created and used. Until the 1950s, mortars were made and utilized in the workplace. Mineral adhesives, typically cement and aggregates (mainly quartz sand), are transported to the job site separately and then manually combined in the appropriate ratio. The wet mortar should be mixed with water before usage. The demand for new building materials and technology increased during the 1950s and 1960s in Western Europe, particularly in Germany and the United States of America [5]. Despite the fact that the first official patent for manufacturing and using dry mix mortars was published in Europe in 1893, the technology based on mixing mortars on-site was gradually supplanted over the years by factory-mixed dry mortars. As a result, it is the only form on the market nowadays. The mortar formula can be controlled in the lab, and the product quality can be greatly enhanced by adding unique additives that in turn change its behavior and performance. Consequently, the product's added value will be raised as well. The ability to create many types of dry mix mortars, each with unique and appropriate properties, for the demands of a particular application, is the fundamental benefit of the ready-to-use mortars. Additionally, by mixing the materials prior to use, this technology enables consumers to prevent mistakes that traditionally occurred when the mortar was created on-site.

4. CEMENT-BASED TILE ADHESIVE

In both modern and historic building, ceramics and tiles are frequently used for internal and exterior decoration. Ceramic floor and wall tiles are highly resistant to abrasion, chemical agents, and water, and they are hygienic and washable as well. Rapid development of the supplementary materials to cling to these coatings is justified by their widespread applications. The commercialization of dry mix mortars with various properties is the result of much study in this area. Cement and sand are the conventional ingredients in tile adhesives. The finished product has important properties thanks to the inclusion of re-dispersible polymer particles in the adhesive mix. The type of the used tiles (for instance, pay attention to large-format floor tiles) and substrate to which they are applied affects the performance, efficiency, and durability of the CTAs. Just before usage, cementitious adhesives should be combined with water and put as a thin layer beneath ceramic or tile. Flexibility, deformability, ease of use, reliability, and appropriate adherence of all types of tiles to all types of substrates are the key characteristics to seek for in an adhesive. Most nations throughout the world have standardized the specifications for cementitious CTAs [6].

5. CLASSIFICATION AND STANDARDS OF CEMENTITIOUS TILE ADHESIVE

The specifications for the CTAs were defined in 2001 with the establishment of the European Standard EN 12004:2001. EN 12004:2001/A1:2002/AC:2002, EN 12004:2007, EN 12004:2007+A1:2012, and EN 12004-1:2017 are the most recent revisions to the standard. The most recent version of the standard with the requirements for CTAs is EN 12004:2007+A1:2012, which is included in the list of European harmonized standards. The official list of harmonized standards published in the Official

Journal of the European Union has not yet included the EN 12004-1:2017 standard, meaning that it cannot serve as the foundation for both evaluation and verification of the consistency of the performance [7].

Additionally, there are a number of ISO 13007 standards for CTAs, which have nearly identical specifications as EN 12004. The terms pertaining to the components, processes, and application characteristics of the CTAs are defined in ISO 13007-1:2010. It specifies the values of performance requirements for all CTAs. Furthermore, they are covered by ANSI (American National Standard Institute) Standard 118.

The mechanical specifications are used to categorize cementitious tile adhesives. Based on the tensile adhesion strength of the adhesives, the EN 12004 standard establishes two primary classifications, i.e., C1 and C2 [8]. The C1 class adhesive cannot be used for tiles entirely made of glass or in locations with considerable thermal stress (balconies, roofs, terraces, etc.). On the contrary, C2 adhesive enjoys the benefit of being used with all kinds of substrates and tiles. The requirements for CTA in accordance with EN 12004: 2007+A1: 2012 are listed in Table 1 [9].

TABLE 1. Characteristics of CTA according to the requirements EN 12004: : 2007+A1:2012

Fundamental Characteristics		
(C1) Normal setting adhesion		
Characteristics	**Requirement**	**Test Method according to EN120004-1**
Initial tensile adhesion strength	≥ 0.5 N/mm^2	
Tensile adhesion strength after water immersion	≥ 0.5 N/mm^2	
Tensile adhesion strength after heat aging	≥ 0.5 N/mm^2	8.3
Tensile adhesion strength after freeze/thaw cycles	≥ 0.5 N/mm^2	
Open time tensile adhesion strength	≥ 0.5 N/mm^2	8.1
Fast setting adhesion (C1F)		
Initial tensile adhesion strength	≥ 0.5 N/mm^2	8.3
Open time: tensile adhesion strength	≥ 0.5 N/mm^2	8.1
All other requirements for C1		
Optional Characteristics		
Special Characteristics		
Slip (T)	≤ 0.5 mm	8.2
Extended open time (E): tensile adhesion strength	≥ 0.5 N/mm^2	8.1
Deformable adhesive (S1): transverse deformation	≥ 2.5 mm	
	≤ 5 mm	8.6
Highly deformable adhesive (S2): transverse deformation	≥ 5 mm	
Additional Characteristics (C2)		
Initial tensile adhesion strength	≥1 N/mm^2	8.3

6. INGREDIENTS OF CEMENTITIOUS TILE ADHESIVE

The properties of the cementitious adhesives can be significantly affected by the type and proportion of the components, mixing, implementation, and curing conditions. In this section, the materials that are regularly used in the composition of cementitious adhesives are reviewed.

6.1. Cement

The hydraulic component of a cementitious system is cement. Utilized as a building material, cement is combined with either fine aggregates to create mortar or with sand aggregates to create concrete.

Cement comes in a variety of forms with different chemical compositions, mechanical characteristics, strengths, and durability.

Portland Cement (PC), which is primarily utilized as a binder in the production of concrete, is the most frequently used cement [10]. According to the ASTM C150 standard, Portland cement contains about 55 (wt. %) of alite or tricalcium silicate (C_3S), 20 (wt. %) of belite or dicalcium silicate (C_2S), 10 (wt. %) of tricalcium aluminate (C_3A), 8 (wt. %) of tetra calcium aluminofrite (C_4AF), 5 (wt. %) of gypsum, and about 2 (wt. %) of sodium and potassium oxide. It should be noted that gypsum is added in order to adjust the setting time; otherwise, cement will be set too quickly [11]. Cements including Portland cement, slag cement, pozzolanic cement, composite cement, and calcium aluminate cement are examples of hydraulic binders. Based on the weight of the dry mix mortar, the amount of cement in the ceramic tile adhesives is typically set between 35 and 50 (wt. %) [12].

6.1.1. Mechanism of Hydration Reactions

Considering the importance of cement behavior in the mechanical properties of CTA, a review is presented on the mechanism of cement hydration reactions in this section. Cement hydration is a complex chemical

reaction between cement and water that leads to the production of a rigid and mechanically resistant material. The progress of these reactions is evaluated based on the setting and curing. Setting and curing are the terms used to describe the initial gradual decline in the cement workability until the mixture is no longer workable and the progressive rise in the mechanical strength. There is no discontinuity between these two processes. When water is added, the reactions that occur are primarily exothermic.

Figure 6 depicts the heat generated as a function of time by the beginning of cement hydration reactions. In the first stage of cement hydration, the temperature rises quickly.

The second phase is referred to as the sleep phase. In this phase, the rate of temperature increment is noticeably lower than that of other phases. The sleep phase takes about one to three hours. The concrete is in a plastic form during this time, enabling transportation to the workplace. The initial setting starts at the end of this phase. In phases III and IV, the concrete begins to harden, and the temperature increases mainly due to the hydration of tricalcium silicate. After 36 hours, Step V begins. As long as water and unhydrated silicates are present, the gradual production of hydration products happens and continues [13].

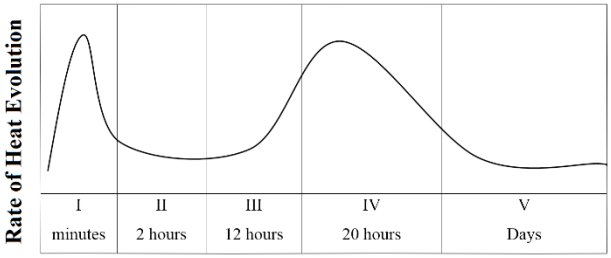

Figure 6. The heat of cement hydration vs. time

A more detailed explanation of hydration reactions is given below. With addition of water, a series of reactions occur. To be specific, ettringite and heat are produced when tricalcium aluminate reacts with gypsum in the presence of water according to the reaction (1).

$$C_3A + 3\ CSH_2 + 26\ H \rightarrow C_6AS_3H_{32},\ \Delta H = 207\ cal/g \quad (1)$$

Ettringite consists of needle crystals that are only stable in solution with gypsum. This composition does not incorporate cementitious adhesive strength.

Heat, hydrated CSH, and hydrated lime are produced in reaction (2) when tricalcium silicate (allite) hydrates:

$$2\ C_3S + 6\ H \rightarrow C_3S_2H_3 + 3\ CH,\ \Delta\ H = 120\ cal/g \quad (2)$$

CSH has a fiber structure with a short network, which greatly contributes to the initial strength of the cement adhesive. Through the consumption of the gypsum (reaction (1)), the ettringite becomes unstable and reacts with residual tricalcium aluminate to form aluminate monosulfate hydrate crystals according to the reaction (3):

$$2\ C_3A + C_6AS_3H_{32} + 22\ H \rightarrow 3\ C_4ASH_{18} \quad (3)$$

Monosulfate crystals are only stable in sulfate-free solutions. In the presence of sulfates, the crystals turn into ettringite, whose crystal size is two and a half times that of monosulfate. An increase in the size causes cracks in the cement exposed to the sulfate attack. Blite (dicalcium silicate) also hydrates to form calcium silicate hydrates and heat according to the reaction (4):

$$2\ C_2S + 4\ H \rightarrow C_3S_2H_3 + CH,\ \Delta H = 62\ cal/g \quad (4)$$

Like the second reaction, calcium silicate hydrates contribute to the cement paste strength. This reaction proceeds more slowly and generates less heat. However, contribution of C_2S to cement paste strength is initially negligible, and it will be ultimately accountable for durability of the PC concrete.

Gypsum and ferrite go through two sequential reactions:

- In the first reaction, ferrite reacts with gypsum and water and forms ettringite and alumina hydroxides, and hydrated lime.
- Ferrite reacts with newly produced ettringite and creates garnet.

Garnets do little more than take up space; they make no contribution to the cement paste strength. Finally, the hardened Portland cement paste includes the following [11, 14-16]:

- Ettringite: 15-20 %
- Calcium Silicate Hydrate (CSH): 50 to 60 %
- Calcium hydroxide: 20 to 25 %
- Pores: 5 to 6 % (in the form of capillary cavities and trapped air)

6.2. Aggregate

The main part in the com position of the tile adhesive is aggregate. For this reason, the aggregate properties have a significant impact on the durability and efficiency of the adhesive mortar.

The properties of aggregates such as mineral and chemical composition, petrographical characteristics, density, hardness, mechanical strength, chemical and physical stability, porosity structure, shape, size, and surface texture are some of the factors that affect the final properties of the adhesive [17]. Cement-based ceramic adhesives contain both coarse and fine aggregates in their composition.

6.2.1. Coarse Aggregates

To make the mortar stronger, aggregates serve as the structural support and reinforcement. By providing bending strength and durability and filling in empty gaps, they improve the density of the system [11,18]. Silica sand, dolomite, limestone, light aggregates (such as perlite, polystyrene, hollow glass spheres), etc. can be used as aggregates in ceramic adhesives. The amount of aggregate is usually reported between 50-70 wt. % based on the total weight of the dry mix mortar [12]. The size of the quartz filler (sand), usually used in the CTA, is up to 0.5 mm. In the case of CTAs intended for large format floor tiles, the sand size up to 1.2 mm is used in part (in the combination with 0.5 mm) [12].

6.2.2. Fine Aggregate (Filler)

Calcium carbonate is the filler that is most frequently used in cementitious tile adhesive. Fine calcium carbonate enhances consistency and workability of the fresh mix. Of note, it should be noted that due to its nature, limestone powder tends to absorb water, thus making the hardened tile adhesive brittle [12].

6.3. Cellulose Ether

Cellulose is a polysaccharide with the chemical formula of $(C_6H_{10}O_5)_n$ that is an organic substance. It is made up of a linear chain of hundreds to thousands of di-glucose units that are joined together by glycosidic linkages.

Cellulose fibers are made up of bundles of parallel, unbranched chains that are joined together to form fibrils by hydrogen bonds between the hydroxyl groups on nearby chains. Hydrogen bonds cause parallel chains to be arranged in bundles, which gives cellulose fibers their high mechanical strength. Amorphous and crystalline cellulose are both possible [19–20].

One of the essential components of the cement-based tile adhesives is cellulose ether. Cellulose ethers are utilized in hydraulic systems as a water retention agent and have a considerable impact on the adhesive qualities. The water retention agent is essential to achieve the optimum workability of the mortar and to regulate the amount of water needed for the hydration of the cement. The mortar acquires the necessary strength, hence protected from cracks by the adhesive cement being properly hydrated. To get the necessary open time to work with the adhesive, the cellulose ether must retain water. Additionally, cellulose ethers enhance the rheological characteristics of mortar. The consistency of the fresh components is also improved by using polysaccharides such as derivatives of starch [11,21].

Alkyl celluloses, hydroxy-alkyl celluloses, and alkyl-hydroxyl celluloses replaced with two or more alkyl or hydroxy-alkyl groups or a combination of two or more cellulose derivatives can all be found in cellulose ethers. For instance, Hydroxypropyl Methylcellulose (HEMC), Hydroxyethyl Methylcellulose (HPMC), Carboxymethylcellulose (CMC), Hydroxyethyl Cellulose (HEC), Hydroxypropyl Hydroxyethyl Cellulose (HPHEC), and Ethyl Hydroxyethyl Cellulose (EHEC) are ether celluloses that are used in the composition of cementitious ceramic adhesives [13, 21–22].

Numerous studies have explored how cellulose ethers can affect the properties of cementitious adhesive. The capacity of the cellulose ethers to interact with cement and bind the cement matrix and aggregates to prevent their separation in the paste was highlighted by Hayakawa and Soshiroda in 1986 [23–24]. Tanaka et al. [25] used an additive containing cellulose ether which can boost the compressive strength while simultaneously increase fluidity and workability.

Polysaccharide derivatives were introduced Yamamuro et al. [26] to investigated include ionic and hydrophobic functional groups that could raise the viscosity of cement solution. Additionally, cellulose ether enhances the bond between the cement and substrate. In cementitious adhesives made from cellulose ether, Ghio et al. [27–28] confirmed an increase in the thixotropy and improvement in the workability of the mortar.

In another study, the relationship between the HPMC viscosities and ceramic adhesive characteristics showed that the absence of ether cellulose in the formulation prevented the adhesive from meeting EN 12004 criteria. Additionally, upon increasing the viscosity of the cellulose ether from 15 Pa.s up to 70 Pa.s, the adhesive qualities and adherence were also enhanced. Further analysis and inspection of the hardened mortar microstructure revealed that the amount of C-S-H phase rose as the viscosity of methylcellulose increased. After combining the adhesive powder with water for the first 24 hours, addition of ether cellulose to the composition lowered the hydration rate of the cement [29].

The additional benefit of the celluloses, especially HEMC and HPMC, is that they stabilize the air bubbles during the mixing stage. Workability depends on the stabilization of air bubbles. Air bubbles, however, weaken the mortar's ability to adhere. The relationship between the adhesive strength and resistance to flexibility is an exponential function of density. Creation of an optimal system with appropriate workability and sufficient mechanical strength is therefore required [30].

There is a significant affinity between the water molecules and cellulose ethers. Each cellulose ether molecule is surrounded by a hydrated sphere that makes the fluid phase become immobile and give cement the ability to retain water. To ensure enough water retention and, as a result, enough water for complete hydration of the cement, cellulose ethers are utilized in the composition of tile adhesives. High water retention also guarantees the continued wettability of the adhesive once applied to the substrate (open time). This matter gains even more significance, especially when it is hot or windy outside [26].

The ability of the cementitious adhesives to resist slipping, particularly on non-horizontal surfaces, is an optional feature. This feature comes from the modified cellulose ethers, which give the fresh mortar paste more consistency by thickening and increasing its viscosity. The viscosity of the mortar is further increased by using modified cellulose ether with a certain molecular weight and a thickening such starch or Polyacrylic Amide (PAA). Additionally, cellulose has a thickening effect on the fresh mortar paste [26].

It should be noted that the delay in cement hydration is one of the additional effects of using these macromolecules in mortar composition.

The chemical composition of the cellulose ether molecule is largely responsible for this delay. According to the observations, portlandite is not developed when ether cellulose is adsorbed on the cement clinker phases. Cellulose ether has a significant impact on the hydrated calcium silicate precipitation, which reduces the number of initial hydrated calcium silicate nuclei and delays the development of a continuous hydrated calcium silicate shell surrounding the tricalcium silicate grain. Finally, it prevents the formation of a dense layer of hydrated calcium silicate that is permeable in the system.

The dissolving rate of calcium aluminate gradually declines when cellulose ether is added to a cement matrix, and ettringite, hence precipitation of calcium hydroaluminate. When compared to hydroxypropyl methyl cellulose, this issue occurs more frequently with HEC [10].

The delay in the cement setting is proportional to the number of methoxyl groups. Therefore, it is essential to employ the optimal amounts of cellulose derivatives to enhance the capabilities of the adhesive without jeopardizing those properties by delaying cement hydration [31].

Water immediately evaporates from the adhesive surface in a fresh mortar. A thin layer of cellulose ether was formed after about five minutes that prevented further evaporation. The initial layer of the mortar is partially dissolved as the water moves from the core to the surface before evaporating. The cellulose ether is brought to the surface of the adhesive by this water flow, where it accumulates over time to the point that the film is no longer dissolved. The adhesive qualities at the mortar/tile contact are gradually diminished by this layer, which prevents tile adhesive from getting wet. Migration of cellulose ether to the surface to create a film is inhibited by the adsorption of cellulose ether on the cement grain, which results in a prolonged setting delay.

However, regulation of the film is also vital because a too thin film dissolves and permits surface evaporation. Creation of this film is necessary to prevent drying of the applied mortar surface. However, as a result of the high concentration of cellulose ether in the pore solution, a thick film decreases the wetting between the tile and the adhesive and the adhesive characteristics.

Cement hydration and latex film production both contribute to the system strength during the adhesive hardening process. The water concentration gradient, which is produced by capillary transport to the substrate, mortar evaporation, and cement hydration, is one of the key characteristics during hardening. Early mortar drying can significantly minimize cement hydration. The capacity of the cellulose ether to hold water and the small size of the pores prevent rapid drying. As a result, the adhesive is strengthened by increasing the concentration of redisperiable polymer and cellulose ether at the contact between the tile and the substrate. On the contrary, the entrapped air in the paste prevents mixing during tiling by creating a film as a result of the migration of the cellulose ether to the surface. The trapped air persists at the tile-mortar interface where it lowers the contact surface and, consequently, the adhesive properties [31]. As a result, optimizing the film thickness is crucial for the CTA characteristics.

6.4. Polymers

The so-called polymer-modified flexible tile adhesives, the second generation of thin-bed tile adhesives, were released on the market in the beginning of the 1980s. This important development in the adhesive technology was made possible by Wacker Chemie's invention of Re-dispersible Polymer Powder (RPP) in 1953. Improved efficiency, flexibility, and adhesion are the key benefits of RPP in the formulation of ceramic adhesives [11]. To improve the stickiness and shear resistance, polymers are added to the adhesive formulations [32]. The tensile strength, plasticity, wear resistance, and flexural strength of the mortar are all enhanced by redistributable polymers, which also produce a suitable degree of flexibility. These polymers also increase the water retention capacity of the mortar and prevent its water evaporation by forming a film. The polymer film closes the pores and cracks in the dried grout, thus preventing water evaporation. Additionally, by forming an additional bond, the polymer strengthens the mechanical properties of the mortar [33]. In the polymer dispersion process during the cement hydration in the adhesive mortar, two hypotheses are proposed. The first theory states that there is no chemical reaction between the polymer and cement components. Upon using polymers, the water amount in the system decreases and leads to the integration of polymer particles, thus causing the gradual formation of a three-dimensional polymer network and increasing the strength and toughness of the adhesive mortar. The second theory postulates that in addition to this occurrence, polymer particles and cement hydration products interact chemically that results in the formation of complexes that either delay or hasten the hydration of the cement system [11,34].

Elastomeric and thermoplastic powders are the two categories into which the re-dispersiable polymers on the

market can be divided. Styrene Butadiene Rubber (SBR) is an elastomeric powder while poly (ethylene-vinyl acetate), poly (vinyl acetate-vinyl verstate), poly (styrene-acrylic ester), and polyacrylic ester are thermoplastic powders (PAE). Examples of polymers that are frequently used in the formulation of ceramic adhesives include vinyl acetate, copolymers of vinyl acetate with ethylene, copolymers of vinyl acetate with ethylene and vinyl ester, copolymers of vinyl acetate with ethylene and acrylic ester, copolymers of vinyl acetate with ethylene and vinyl chloride, copolymers of styrene acrylic ester, and copolymers of styrene-1. The flexible butadiene and rigid styrene chain in the SBR structure increases adhesion, durability, and mechanical qualities in the concrete mortars [35–38]. EVA, or poly (ethylene-vinyl acetate), is another type of re-dispersible polymers that is frequently used due to its satisfactory working with the cement base system [39–41]. VA/VeoVa, often known as poly (vinyl acetate-vinyl versatate), is another polymer that has drawn academic attention. The polymer, with its remarkable resistance in alkaline environments, gains three side chains of the alpha alkyl molecule due to the presence of the versatate group [42–45]. The compressive and tensile strengths as well as the water retention effect improve with a rise in the poly (styrene-acrylic ester) or SAE to cement ratio [46–47]. Additionally, polyacrylic ester, or PAE, proved to have adequate workability and improved mechanical characteristics [48–49].

The mechanical properties of polymers change drastically at the glass transition temperature (T_g) due to the molecular motion. Below T_g, polymers are relatively rigid, inflexible, and brittle with no translational or rotational movement of the atoms in the chain while above it, they are soft and flexible. The main advantages of RPP in thin-bed tile adhesive are [31]:

- Improved adhesion between the substrate and adhesive;
- Greater flexibility facilitates use of adhesive for big tiles and lowers the shear stress on the substrate, tile adhesive, and tiles.
- Improvement in the rheological characteristics facilitates easier mixing, workability, and adhesive wetting of tiles. Copolymers of Ethylene and Vinyl Acetate (EVA) or styrene and butyl acrylate are the typical RPPs used for tile adhesive. Between 0 and 5 % of CTA contains redistributable polymer powder [13,21].

In their study, Jenni and et al. confirmed that the RPP could boost the adhesive strength of the mortar owing to the impact of polymer on the microstructure and adhesive strength of the cement tile adhesive. Microstructural analyses demonstrate that the polymer can improve the adhesive capabilities when entirely and uniformly dispersed in the cement-polymer matrix. On the sample surface, containing cellulose ether, polymer films with the width of 10-100 μm were detected. Therefore, they came to the conclusion that the formation of this film in the entire matrix was the reason for enhancing the adhesion strength of the adhesive. The type of re-dispersible polymer utilized (SA, EVA, or VC) affects the tendency to create cellulose ether-polymer composite films and their morphology [32]. In a cement (CEM 1 32.5R) and sand combination, Schulze [50] examined the effects of utilizing SAE (polystyrene-acrylic ester) and EVA (poly (ethylene-vinyl acetate)) in both internal and external weather conditions. After 28 days in the open, the adhesion strength of the EVA-modified mortar was higher than that of the SAE-modified mortar and higher than that of the conventional cement-sand mixture. All mortars showed a steady rise in their adhesion strength over the course of 10 years, and all samples attained their maximum strength. However, compared to the initial amount of the EVA-modified mortar, the tensile adhesion strength of the control sample (standard cement and sand mixture) was considerably low. Over 10 years, no increase in the strength of the control or un-modified sample was reported in indoor condition. Due to the mortar's ability to keep a suitable amount of water for the cement hydration, the adhesives that contained EVA and SAE in their composition exhibited similar performance, and their adhesion strength increased during 10 years. The aggregates are kept together and adhere better as a result of the application of polymer powders. Similar to the previous study, it was found that the polymer could distribute water throughout the system and prevent the polymer from separating water from the adhesive paste. It could also retain water in the adhesive composition and reduce the amount of water required to prepare the adhesive paste [43].

6.5. Accelerator

Hydraulic systems typically use the accelerator. Accelerators speed up the hydration process and shorten the setting period of the cement, hence an increase in the tensile strength of the adhesive. There are two types of additives: organic and inorganic. Chlorides, such as calcium, sodium, and potassium chlorides, nitrites, such as sodium nitrate and calcium nitrate, sulfates, such as sodium sulfate and calcium sulfate, thiocyanates, like calcium thiocyanate and sodium thiocyanate, hydroxides, include sodium hydroxide, potassium hydroxide, and calcium hydroxide, carbonates such as calcium carbonate, sodium carbonate, Amines like diethanolamine and triethanolamine, calcium salts, and organic acids like calcium formate, calcium acetate, and maleic anhydride are examples of organic substances. According to reports, the accelerator should be used in the range of 0.1 and 0.3 wt. % [21].

6.6. Retarder

Cementitious ceramic adhesives use a retarding

ingredient. The main task of the retarders is to postpone cement hydration so that workers have adequate time to manipulate the paste in an open area [18]. Mineral retarders like lead and zinc oxides, phosphates, magnesium salts, fluorides, and borates are common. Examples of organic retarders are the Na, Ca, and NH_4 salts of lingosulfonic acids, adipic acid, citric acid, tartaric acid (together with citric acid), gluconic acid, heptonic acid, succinic acid, and polysaccharides. The retarders included in the formulation of cement adhesives are saccharides and their salts such as glucose, sodium gluconate, fructose, galactose, sucrose, xylose, ribose, arabinose, sucrose, mannose, oligosucrose, dextran, lignosulfonates, phosphoric acids and their salts, and boric acid. Followed by creating a compound with monosulfates, citric acid functions as an accelerator in the early stages of hydration before acting as a retarder. According to the reports, commercial lignosulfonates without sugar yielded good results in terms of delaying the hydration of tricalcium aluminate (C_3A) and tricalcium silicate (C_3S). Zinc oxide is an inorganic retarder that slows the hydration of C_3S but has no effect on the hydration of C_3A or gypsum [21]. Retarders are typically added to the adhesive compositions in amounts ranging from 0.01 to 0.05 wt. % [13].

6.7. Fibers

Fibers are frequently used to strengthen and prevent creep in cementitious materials. The significant effect of the fibers is to bridge at the crack tip to resist crack propagation in the cement matrix. The connection of the fiber to cement paste is an essential factor that affects the performance of fiber-reinforced cement composite. The bonding energy (adhesion) between these materials includes surface interactions (chemical bonding) and mechanical interactions (interlocking). Fibers can be classified into two groups depending on their average length: long fibers with a higher aspect ratio between 200 and 500 are mainly used to strengthen the mortar while short fibers with the ratio of the overall dimensions between 20 and 60 affect the characteristics of the fresh mortar. A typical dose of macro fiber with more than 40 mm in length is 3-8 kg/m^3. The microfibers are 6-12 mm long with the typical dosage of 0.6-1.0 kg/m^3. Macrofibers are used to increase the strength of the tile adhesive [51]. Polypropylene fibers are used commonly in cementitious systems.

6.8. Other Additives

Thickening agents, secondary water retention agents, wetting agents, defoamers, superplasticizers, dispersants, surface activating agents, calcium chelating agents, calcium complexing agents, and water repellants are the additives that are used in the composition of tile adhesives [52]. Plasticizers, superplasticizers, dispersants or water reducing agents are additives that disperse binder particles and increase the fluidity of the binder (cement or plaster). The superplasticizer improves the fluidity of the mortar and increases the opening time; it also has a positive effect on the mechanical strength of the adhesive [53]. Among the water-reducing agents are the melamine-based agents, lignin-based agents, and poly-carboxylate-based compounds, to name a few [21]. The defoamers often include polyether, silicone, alcohol, mineral oils and non-ionic surfactants. The usual amount of defoaming additives is between 0.2-4 % by weight (based on dry mix mortar). Gelatin, polyethylene glycol, lignin sulfonate, naphthalene-sulfonate, polycarboxylate ether, polystyrene sulfonates, calcium salts from organic acids such as calcium formate, bentonite, montmorillonite, polyamide fibers, metallic aluminum, fibers Propylene, polyvinyl alcohol, vinyl acetate-based polymers, styrene, butadiene, ethylene, and etc. are different types of the additives of cementitious ceramic adhesives [21]. A summary of the most general additives used in the CTAs is given in Table 2.

Cementitious ceramic adhesives are categorized into two classes of C1 and C2 in EN 12004, as previously discussed. The amount of polymer combined with other ingredients in the adhesive composition is the primary difference between C1 and C2 tile adhesive. Table 3 gives some recommendations for the composition of ceramic adhesives based on cement. To enhance the qualities of their formulation, a majority of producers use composition in this range together with other additions.

It has been claimed that the CTA composition occasionally includes as many as 15 different types of components [18].

TABLE 2. The most common additives in CTA composition cement-based ceramic adhesives

Additive	Example
Redispersible Polymer	EVA, SBR, SAE, PVA
Water Retention	HPMC, HEMC
Superplastisizer	Polycarboxylate, Melamine, Lignin
Accelerator	Calcium Formate
Retarder	Glucose, Lignosulfonate
Fiber	Polypropylene
Defoamer	Mineral Oils

TABLE 3. The general formulation of the cement-based ceramic adhesives

Ingredient	Example	Amount	
		Class C1	Class C2
Binder	Portland Cement	30-50	30-40
Aggregate	Silica Sand	45-70	45-60
Filler	Calcium Carbonate	5-10	5-10
Redispersible Polymer	EVA, SBR, SAE	0-3	3-6
Water Retention	HPMC	0.2-0.5	0.2-0.5
Additives	Accelerator, Retarder, Defoamer,…	< 2	< 2

7. EVALUATION OF THE PERFORMANCE OF THE CEMENTITIOUS CERAMIC ADHESIVE

Assessment and verification of constancy of performance (AVCP) of CTA is carried out considering the EN 12004:2007+A1:2012. The conditions of these tests are summarized below [54].

7.1. Open Time

The open time test is designed to study the behavior of the adhesive after application to the substrate and exposure to air. Applying the adhesive to a large surface requires more time and then, the adhesive will be exposed to air. As mentioned, one of the crucial components of the adhesive is cellulose ether, whose main feature is the retention of water in its molecular structure. This feature is combined with the formation of a thin layer on the surface to prevent water evaporation and increase the wettability of the adhesive.

Storage conditions: 27 days in standard conditions (temperature 23 ± 2 °C and humidity 50 ± 5 %).

7.2. Initial Adhesion

The purpose of this test is to evaluate the performance of an adhesive that is not subjected to particular stress during its working life, for instance, inside the building.

Storage conditions: 28 days in standard conditions (temperature 23 ± 2 °C and humidity 50 ± 5 %).

7.3. Heat Aging

In hot climates, the temperature on the building facade that is exposed to sunlight can easily reach 70 °C in the summer, which leads to rapid drying, rapid setting, and fracture of the cementitious tile adhesive. These application conditions have a significant effect on the long-term safe adhesion of tiling. The purpose of this test is to identify the vital factors for tiling under such difficult conditions and find a solution to enhance the durability and permanence of tiling.

Storage conditions: 14 days in standard conditions, then 14 days at 70 °C, and then one day in standard conditions. When the temperature of the plates reaches 23 °C, the tiles are pulled from the concrete plate until they are removed.

7.4. Immersion in Water

Adhesives that are used for adhering tiles on the exterior of the building or in wet facilities such as swimming pools and bathrooms, necessarily have high resistance to water. In other words, water resistance is defined as the adhesive ability to withstand contact with water without fracture. Of note, this term should not be confused with the term "waterproof".

Storage conditions: 7 days in standard conditions plus 21 days immersion in water. This test is performed immediately after the tiles are removed from the water, while still wet, to best simulate actual conditions.

7.5. Freeze/Thaw Cycles

Water that has penetrated the tile during installation may expand in volume as a result of freezing. As the freezing and thawing cycles continue, the mechanical stresses caused by this volumetric shift will grow and become more harmful. The tile body as well as its surface (especially if it is glazed) and the adhesive (which in some cases results in the loss of adhesion) can all be destroyed by stress.

One of the crucial requirements, especially for use in areas with high humidity levels, is the ability to withstand these cycles without suffering significantly from loss in adhesive strength.

Storage requirements: 7 days in standard conditions plus 21 days immersion in water plus 25 cycles of freezing and thawing cycles: 2 hours at -15 °C / 2 hours at 15 °C.

8. CHALLENGES AND THE FUTURE PATH OF CERAMIC TILE ADHESIVE

Like any other technology, cement-based ceramic adhesives encounter a number of difficulties. When using tile adhesive, the following factors can hinder the desired outcome:

1. The change in the shape of the mortar consisting of the adhesive, compared to the ceramic tiles on it as a result of shrinkage;
2. Different displacements as a result of heat, humidity, or other effects occur between the ceramic tile, substrate, and adhesive which devastate the system;
3. Deterioration of the cement that supports the

adhesive;
4. Inadequate surface cleaning;
5. Structural movements such vibrations and settling issues;
6. Inappropriate material selection.

Some recommendations to prevent these flaws and obliterations are given in the following:

1. Appropriate material selection based on the size and efficiency;
2. Designing compatible structures, such as sufficient drainage;
3. Appropriate and right installation techniques. According to the reports, wind, rain, humidity, and attack of pollutants on the outside tiling systems of buildings would weaken the adhesive strength of the ceramic adhesive that leads to the eventual destruction of the system [55].

A market analysis states that the value of the ceramic adhesives market was 15.08 billion dollars in 2018 and is predicted to elevate up to 40.73 billion dollars by 2026 [56]. The market size of ceramic adhesives may be difficult to estimate, but it is evident that CTAs will be a major component of the construction industry in the years to come. Additionally, it appears necessary to run evaluation programs, like inter-laboratory comparisons, to guarantee the proper performance of the product and evaluation methods as well as the accuracy of the used equipment in order to advance the market for these products and their sustainable development.

9. CONCLUSION

The present study aims to present an overview of the CTAs whose composition has an impact on its adhesion qualities. Re-dispersible Polymer Powder (RPP) and other cementitious constituents interact with cement components to improve their physical and mechanical properties such as increased adhesion strength, reduced shrinkage, and low water absorption. Another component that significantly affects the CTA characteristics is cellulose ether. The RPP/CE decision has a significant impact on the end-use values, i.e., whether they are in the fresh or hardened form. The mortar viscosity, setting time, and film formation were all affected by the CE concentration in the pore solution in the fresh condition. The dry tensile adhesion strength was enhanced by CE film in their hardened state, which also prevented evaporation at the tile-mortar interface. The thickness of the CE/RPP layer also had an impact on the tensile strength after heat aging or immersion in water. Increasing the amounts of polymer and cellulose ether content in the system could often improve adhesion after heat aging. However, in contrast to the situations with the smallest amounts of these contents, such an increase could shorten the open time. The CTA formulation according to the desired properties based on the EN12004:2007+A1:2012 could be optimized by using the various additives.

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Original Research Article

$Zn_xCo_{3-x}O_4$ Hydrothermally Mesoporous Nanoparticles (ZCH): Structure, Optical, and Surface Analysis

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ABSTRACT

In this research, cobalt oxide solid solution nanoparticles with different molar percentages of zinc content (2.5, 5, 7.5, 10, 15, 20, 30 mol %) were synthesized through hydrothermal method. Cobalt nitrate and zinc nitrate were used as the sources of cobalt oxide and zinc contents in this research. In order to investigate the structural properties, the chemical state, optical, photocatalytic properties as well as the microstructure of the synthesized nanoparticles were characterized based on the XRD, BET-BJH, UV-Vis, XPS, TEM, and FESEM analyzes. The results of the X-ray phase analysis showed that addition of this content to the structure of cobalt oxide led to a decrease in the crystal size. The crystallite sizes of the pure and doped samples were about 9.48 nm and about 8.8 nm, respectively. According to the FESEM images, the particle size of the pure sample was in the range of 20-40 nm, and that of the doped ZCH-300 sample (10 % Zn) in the range of 20-30 nm. The specific surface areas (BET) of the pure sample and the sample with 10 % zinc were about 75 m^2/g and 92 m^2/g, respectively. Compared to the pure CH nanoparticles Doped Co_3O_4 (CH), mesoporous nanoparticles were observed to have the highest photocatalytic activity. The photocatalytic analysis results showed that the highest degradation percentage of the solution, i.e., 10.6 ($\eta_{ZCH-300}$ = 10.6 %), was obtained in the presence of the doped sample with zinc cation (10 % Zn).

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1. INTRODUCTION

Cobalt oxide (Co_3O_4) is a p-type semiconductor. In recent years, considerable attention has been draw to the photodegradation of color pollutants due to their low cost, excellent chemical, and physical stability [1]. Cobalt oxide nanomaterials are characterized by extraordinary optical, electrical, and magnetic properties [2] and are used for a variety of applications such as gas sensors [3], supercapacitors [4], lithium-ion batteries [5,6], and energy storage devices [7,8]. The behavior of nanoparticles depends on their structural morphology, specific surface area, and structural porosity. Nanoparticles can be prepared through different methods such as sol-gel, hydrothermal, and chemical reduction. Zhao et al. [9] investigated the Co_3O_4 nanostructures in the form of nanowires, nanorods, and spherical nanoparticles using the hydrothermal method to degrade methyl orange dye under ultraviolet radiation. Chen et al. studied the hollow microspheres of Co_3O_4 during a two-

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step process to degrade methyl orange dye under ultraviolet radiation [10]. The photocatalytic properties of Co_3O_4 are not suitable due to the high rate of electron-hole pair recombination in this structure. Further, some methods such as the particle size control [11] or morphology control [12,13], non-metallic dopant or metallic dopant such as Fluorine [14] and Manganese, Nickel or Manganese [15,16] were particularly investigated. Doping in the semiconductor fabrication is one of the methods that increases its photocatalytic performance. The purpose of doping is to improve the photocatalytic properties of nanoparticles. In a chemical co-precipitation method study, Hitkari et al. [16] investigated the effect of Cr dopant (1 and 5 %) on the physical properties of cobalt oxide nanoparticles. They reported that 5 % Cr in the structure of cobalt oxide had a better photocatalytic efficiency than the pure sample. The previous studies in this field were taken into account and to the best of the authors' knowledge, no research has been done on the hydrothermal synthesis of ZCH (Zn doped cobalt oxide) mesoporous nanoparticles so far. To this end, a series of Zn doped Co_3O_4 nanoparticles were prepared with different Zn contents (code: ZCH-2.5 % Zn, ZCH-5 % Zn, ZCH-7.5 % Zn, ZCH-10 % Zn, ZCH-15 % Zn, ZCH-20 % Zn, and ZCH-30 % Zn).

The effect of the Zn content on the structural, photocatalytic, and optical properties of the synthesized Co_3O_4 mesoporous nanoparticles was also studied. In order to investigate the photocatalytic properties, the degradation of methylene blue dye solution under visible light irradiation in the presence of synthesized nanoparticles was taken into consideration.

2. MATERIALS AND METHODS

2.1. Raw Materials

In this research, Cobalt nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), ammonium fluoride (NH_4F), and urea (CH_4N_2O) were used as the precursors materials. Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) was also used as the precursors of the Zn content. All the raw chemicals are analytical-grade reagents that were purchased from Merck Company and used as received without any further purification. In addition, organic methylene blue solution was used for photocatalytic activity.

2.2. Experimental Procedure

In this research, Co_3O_4 (CH) and doped (ZCH) samples of mesoporous nanoparticles were synthesized by a simple and facile hydrothermal route. Briefly, 60 ml of distilled water, 0.655 g (2.25 mmol) of $Co(NO_3)_2.6H_2O$, 0.676 g (11.25 mmol) CH_4N_2O, and 0.167 g (4.5 mmol) NH_4F were mixed together in beaker and magnetically stirred at 25 °C (R.T.) for 20 min.

The thoroughly mixed precursor was then transferred to a 100 ml Teflon-coated stainless-steel autoclave, which was thoroughly sealed and subsequently heated in an electric oven at 150 °C for four hours to precipitate. After cooling down to room temperature, the prepared precipitate was removed by centrifugation and washed three times with distilled water and absolute ethanol, respectively. Of course, after each centrifuge step, the precipitate was formed in ultrasonic for five minutes. The product was dried in air at 60 °C for 12 hours. Finally, the dried precipitate was calcined at 300 °C for two hours. Zn doped Co_3O_4 nanoparticles (ZCH) were obtained in the same process, except that an appropriate amount of $Zn(NO_3)_2.6H_2O$ was added as a source of Zn^{2+} ions (2.5, 5, 7.5, 10, 15, 20, and 30 % Zn).

2.3. Nanoparticle Characterization Methods

The synthesized samples were evaluated using different techniques. Phase analysis of the synthesized sample was performed using X-ray diffraction (XRD, Philips, MPD-XPERT with Cukα radiation, λ= 0.154 nm). The optical absorption spectra, photocatalytic degradation, and band gap energy (E_g) of the synthesized nanoparticles were measured using the spekol-2000 spectrophotometer in the wavelength range of 200-800 nm. The surface area and pore size distribution of the samples were determined by a BELSORP measuring instrument (BELSORP-mini, JAPAN, INC) using nitrogen gas adsorption-desorption technique at 77 K.

Later, X-ray Photoelectron Spectroscopy (XPS) measurements were performed on a VG ESCALAB 210 XPS system with Mg Kα (1253.6 eV) source. All the binding energies were referenced to the C 1s peak at 284.6 eV of the surface adventitious carbon. The morphology of the mesoporous nanopowders was studied using Field Emission Scanning Electron Microscopy (FESEM, MIRA3-TESCAN) with an accelerating voltage of 10-15 kV. High Resolution Transmission Electron Microscopy (HRTEM) was performed on a Jeol-JEM 2011 system operated at 200 kV.

2.4 Photocatalytic Activity

The photocatalytic degradation of organic pollutants by the samples was evaluated by the degradation of methylene blue (MB) as a model pollutant solution under visible (250 W) light irradiation. The photocatalytic experiment was carried out by taking 0.1 g of each sample in 50 ml MB solutions (10 ppm). Prior to the light irradiation, these solutions were magnetically stirred for 30 min in a dark place to achieve the adsorption-desorption equilibrium. The above solutions were irradiated with light and after every 20 min, a 3 ml sample of the solution was taken from which, the catalyst was separated by centrifugation to obtain a clear liquid. The photodegradation rates of the MB solution at the given intervals of irradiation was analyzed using a Ultraviolet–visible (UV-Vis) spectrophotometer. The degradation

percentage of MB, which represents the photocatalytic efficiency of the samples, can be determined by Equation (1).

$$\eta = [1-A_t/A_0]\times 100 \quad (1)$$

where η is the photocatalytic efficiency of MB, A_t the absorption after radiation, and A_0 the absorption before radiation [17].

The energy band gap corresponds to the absorption limit that can be roughly evaluated using the following equation:

$$E_g\ (eV) = 1240/\lambda_{edge} \quad (2)$$

where λ_{edge} represents the absorption limit of the semiconductor. Here, λ_{edge} can be extracted from the absorption spectrum by determining the first derivative of absorbance with respect to the wavelength near the absorption edge and finding the point at which the derivative spectrum reaches its minimum value**.** This point is in fact the reflection point of the absorption curve. The tangent line of the absorption curve at the reflection point intersects with the x-axis on which absorbance reaches 0 and indicates λ_{edge}.

3. RESULTS AND DISCUSSION

3.1. Phase Analysis of CH and ZCH Samples Calcined at 300 °C

The crystal structure and crystalline phases of the pure and doped samples with different percentages of Zn content were investigated using XRD analysis, the results of which are given in Figures 1 and 2. The crystal peaks at the diffraction angles (Figure 1) of 31.1°, 36.7°, 38.6°, 46.8°, 55.6°, 59.4°, and 65.2° are attributed to the crystal plates with Miller index, the (220), (311), (222), (400), (422), (511), and (440) planes of the cubic spinel Co_3O_4, respectively.

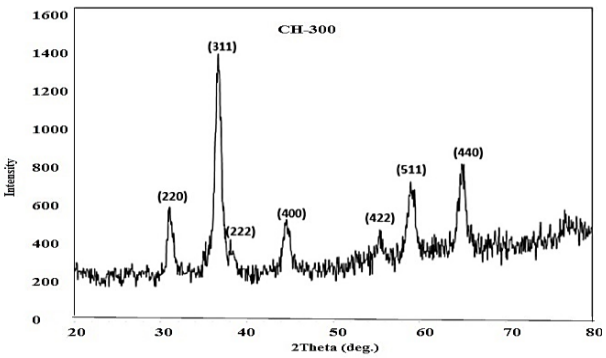

Figure 1. XRD pattern of pure Co_3O_4 (CH) sample after calcination at 300 °C for 2 h

The XRD pattern of all samples corresponds to the JCPDS card no.:43-1003 [18]. The peaks of the synthesized ZCH sample (Figure 2) in the presence of Zn content (solid solution up to 10 % Zn) are similar to those of the pure sample. In the doped samples, the crystal peaks shift to lower angles, which can be attributed to the ionic radius of Zn^{2+} (0.74 Å) which is larger than Co^{3+} (0.6 Å).

Followed by addition of Zn cation up to about 10 %, a peak shift to the lower angles in the Co_3O_4 lattice in the XRD results was observed; however, with the addition of a higher percentage of Zn cation (Zn > 10%), formation of a solid solution of Co_3O_4-ZnO was witnessed.

In the samples with lower than 10 %, no secondary crystallized phase (ZnO phase, JCPDS: 36-1451) were observed in the XRD patterns of the ZCH samples (Zn < 10 %), suggesting that the Zn ions were well incorporated into the Co_3O_4 lattice (Figure 2).

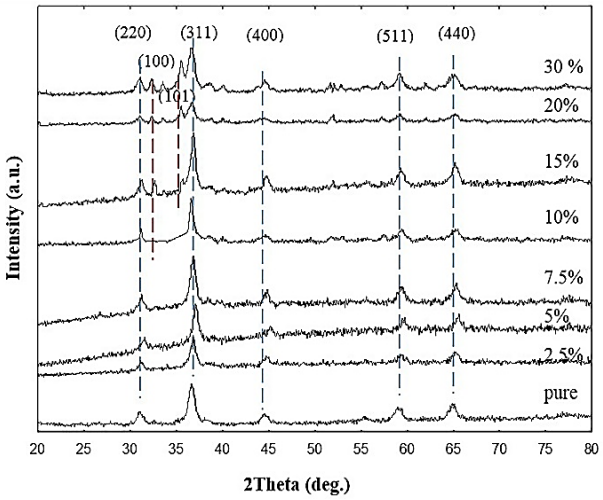

Figure 2. XRD patterns of $Zn_xCo_{3-x}O_4$ (ZCH) samples after calcination at 300 °C for 2 h (Blue Line: Co_3O_4, Red line: ZnO)

3.2. BET-BJH and XPS Analysis of CH and ZCH Nanoparticles

The specific surface area (BET) and porosity of the pure cobalt oxide (CH) sample and ZCH-300 (10 % Zn) calcined at 300 °C were investigated using nitrogen adsorption-desorption isotherm.

The hysteresis loop is compatible with type IV for both CH (Figure 3a) and ZCH (Figure 3c) samples according to the AUPAC classification which confirms mesoporous characteristic of the prepared samples. A comparison was further made between the two calcined samples at 300 °C and consequently, the values of the specific surface area (BET) for the CH sample were calculated as 75.1 m^2/g and 93.2 m^2/g for the ZCH sample, indicating that the sample in the presence of content had a smaller particle size than the pure sample. The shape of the pore is H4 type with a narrow opening porosity with uniform channels in the lattice where the structure of these

porosities is mesomatically porous. In the presence of Zn content (ZCH), these channels are arranged spherically and cylindrically, and the hysteresis loop represents the mesoporous material.

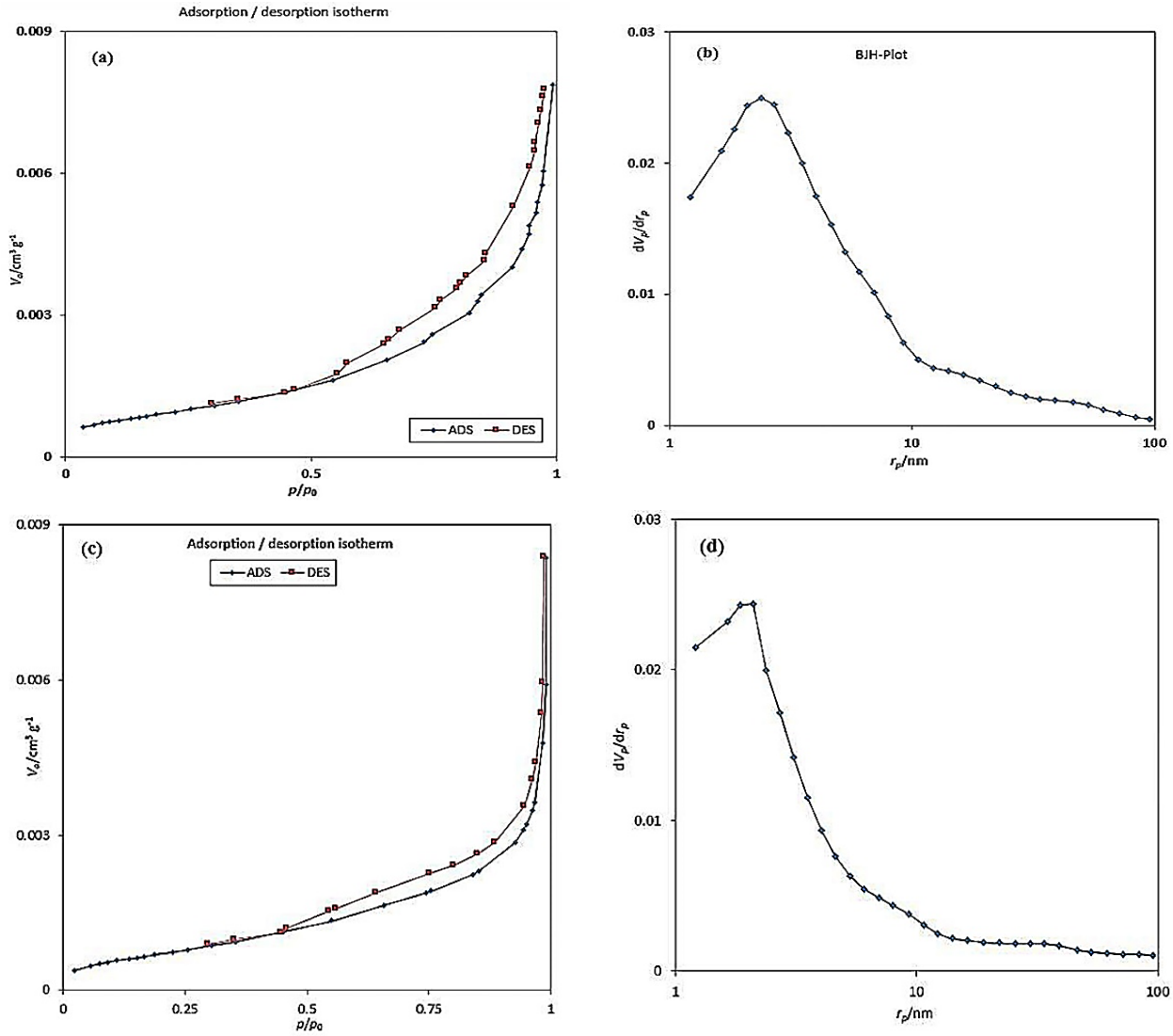

Figure 3. N2 physisorption isotherms (BET) and pore size distribution (BJH) of CH (a,b) and ZCH (c,d) hydrothermally mesoporous nanoparticles calcined at 300 °C

According to the BJH adsorption diagram (Figures 3b,d), the average pore diameters in the CH and ZCH sample are 14.8 nm and 14.2 nm, respectively. Of note, BJH curve for both samples (Figure 3b,d) include a high percentage of mesoporous particles with a small percentage of microporous and macro-porous particles [19]. XPS studies were carried out to determine the chemical composition, surface element composition, and chemical valance states of the synthesized samples. The results of these analyses are reported in Figure 4 on a wide scan. Figure 4a illustrates the broad-spectrum photoelectron spectrum of pure (CH-300) and doped (ZCH-300) samples. Figure 4a shows the presence of Co, Zn, O, and C elements. Figure 4b demonstrates the high-resolution Co 2p spectra. The peaks at 780 and 794.4 eV are attributed to the cobalt cation with the valences of 3 (Co^{3+}) and 2 (Co^{2+}) [20].

Figure 4c shows the high-resolution Zn 2p spectrum of the ZCH sample. The two peaks at 1044.8 and 1021.2 eV are attributed to Zn $2p_{1/2}$ and Zn $2p_{3/2}$, respectively, indicating the presence of a Zn cation with the valence of +2 (Zn^{2+}) [21].

The high-resolution O 1s spectrum in Figure 4d can be further subdivided into two suitable peaks at 530.5 eV and 531.6 eV, which confirm the presence of lattice oxygen (O_L:Co-O) and surface oxygen (O_H:O-H) on the surface [22]. The peaks of Co 2p, O 1s in the XPS spectrum of the ZCH compound are indicative of the

presence of oxygen vacancies, which is useful for the photocatalytic process because it leads to the separation of the electron-hole pair.

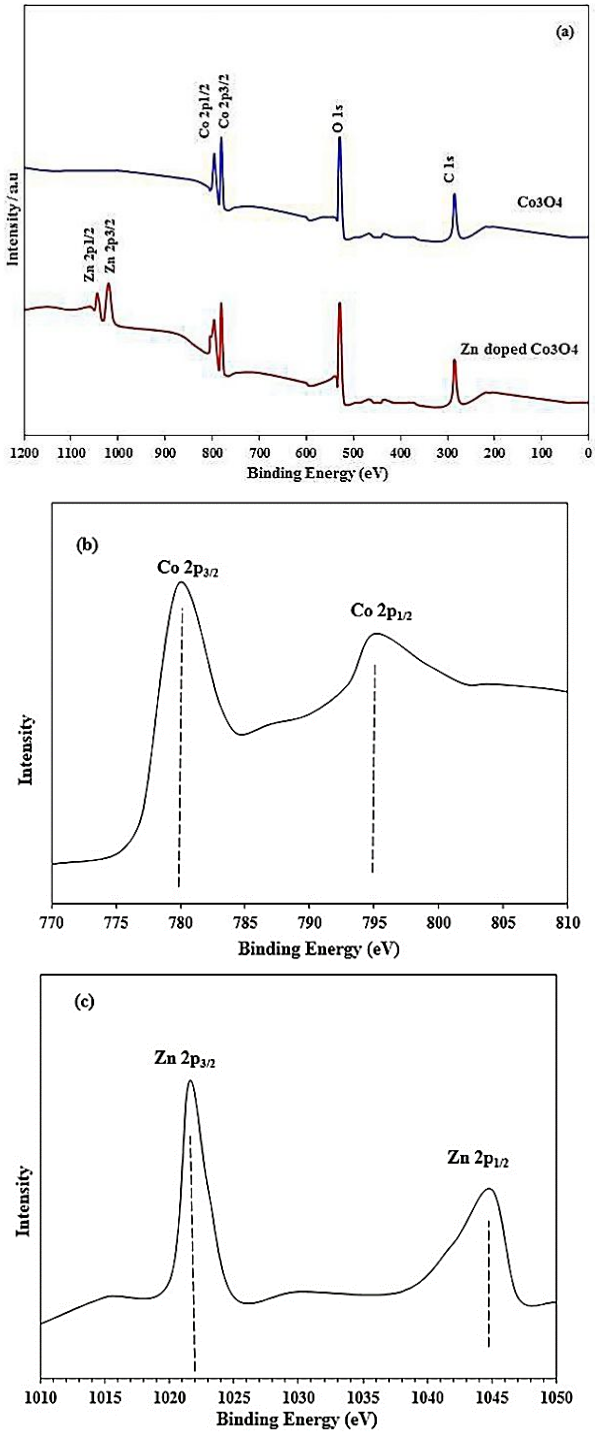

Figure 4. XPS spectra of the pure Co_3O_4 and Zn doped Co_3O_4 mesoporous nanoparticles, scanned in (a) Broad scan XPS analysis of Pure Co_3O_4 and Zn doped Co_3O_4 sample, high-resolution XPS spectra of (b) Co 2p, (c) Zn 2p, and (d) O 1s spectra for ZCH sample calcined at 300

3.3. UV-Vis analysis of CH and ZCH Samples

Photocatalytic degradation of methylene blue dye solution in the presence of the pure sample (CH) and samples with different percentages of Zn content (ZCH) were prepared for spectrophotometric analysis. The analysis results are reported in Figures 5a,b and Table 1.

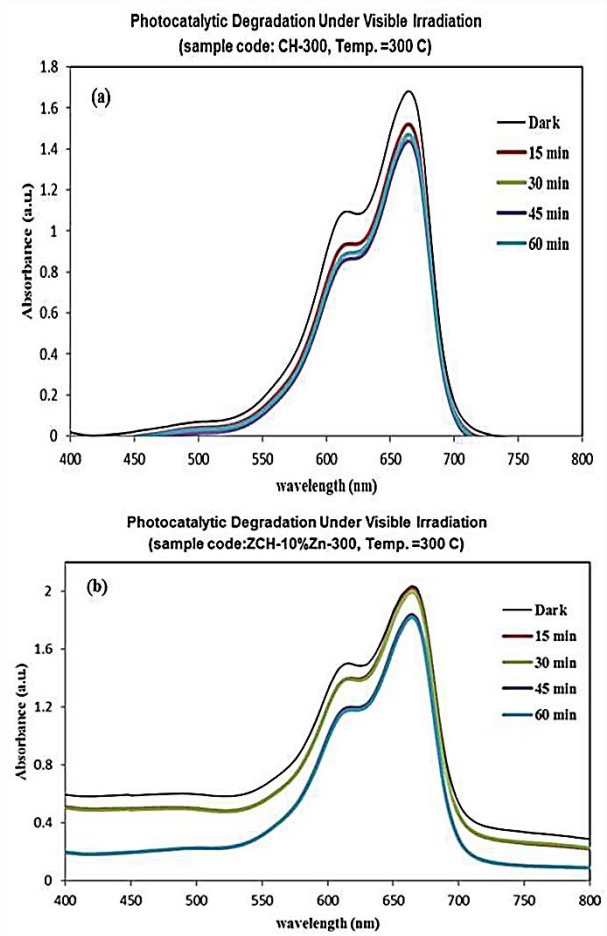

Figure 5. (a) Photocatalytic degradation spectra of CH-300 nanoparticles, (b) ZCH-300 nanoparticles under visible light irradiation time (1h)

TABLE 1. Photocatalytic activity of ZCH samples under visible light irradiation

Samples	η %
ZCH-2.5 %	5.25
ZCH-5 %	10.22
ZCH-7.5 %	6.62
ZCH-10 %	10.6
ZCH-15 %	3.34
ZCH-20 %	4.54
ZCH-30 %	5.29

Figure 5a shows the degradation of MB solution in the presence of pure cobalt oxide (CH-300) at 300 °C under visible light irradiation. The degradation percentage of

the MB dye solution at this temperature is about 12.7 %. The photocatlytic degradation in the presence of doped samples with different percentages of Zn cation was measured, and the UV-Vis spectrum of ZCH-10 % Zn sample was reported as one of the samples with higher photocatalytic efficiency than that of other samples with other percentages in Figure 5b. As observed in Figures 5a,b, after different irradiation times (t = 15, 30, 45, and 60 min), the amount of adsorption (A_t) in the solution decreases, indicating an increase in the photocatalytic efficiency under visible irradiation at different times.

The results of this test for all doped samples are reported in Table 1. The highest degradation percentage of the solution was obtained in the presence of the sample doped with zinc cation (10 % Zn) which was equal to 10.6. The reason for the photocatalytic degradation of the dye solution in the presence of Zn content sample, compared to the pure sample, is probably the non-crystallization of the cobalt oxide structure in the presence of Zn content calcined at 300 °C. For this reason, we will probably need to increase the calcination temperature for calcination of the doped sample.

A simplified Langmuir–Hinshelwood (L–H) kinetic model (Equation (3)) was used to describe the photocatalytic degradation rate of MB by plotting the graph of −ln(C/C0) versus time, t [23].

$$-\ln(C/C_0) = kt \quad (3)$$

where C_0 and C are the MB concentrations in solution at times 0 and t, respectively, and k is the apparent first-order reaction rate constant. In the above equation, k can be calculated by plotting $\ln(C_0/C)$ in terms of t and calculating its slope.

In this research, only the reaction rate constant (k) of the photocatalytic samples was calculated in the form of the following numbers. According to these numbers and results of photocatalytic activity, the doped sample (ZCH (10 % Zn)) has a higher rate constant, which is in accordance with the results of photocatalytic decomposition and is a confirmation of the results of photocatalytic decomposition.

Photocatalytic degradation (η) and apparent first-order reaction rate constant (k) of MB solution in the presence of ZCH (10 % Zn) sample calcined at 300 °C under visible light was investigated. Based on the obtained results, it can be concluded that if this parameter (k) takes a higher value, it will have better photocatalytic properties (CH-300 sample: k = 0.0086 min^{-1} and ZCH sample: k = 0.0034 min^{-1}).

Repetition test for the best sample with higher percentages of photocatalytic degradation (ZCH-300, 10 % Zn) was done for six times, the results of which are shown in Figure 6 that confirms the reuse of the catalyst nanoparticles doped with Zn cation (10 %) for the degradation of MB solution during an experiment for six repetitions. Each experiment was performed under the same conditions of initial concentration of 50 ml MB solution (10 ppm), 0.1 g ZCH with the Zn concentration of 10 mol %, and irradiation time of one hour.

The photodegradaion efficiency values were obtained as 10.6 %, 9.3 %, 8.2 %, 7.4 %, 7.1 %, and 6.7 % for the first to the sixth runs, respectively. Apparently, after the sixth time of the experiment, the percentage of photocatalytic destruction decreased by about 36 %, indicating that after each experiment repetition, a reduction was observed in the Photocatalytic degradation probably due to the deactivation of some active surfaces on the photocatalyst surface.

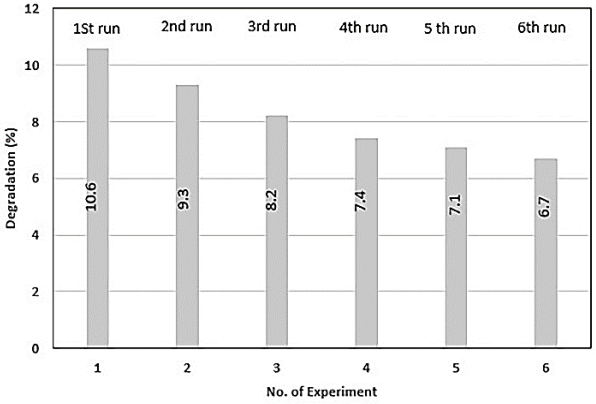

Figure 6. The reproducibility of the ZCH-300 catalyst for MB photodegradation for six cycles)

The optical band gap energies of the pure (CH-300) and doped samples (ZCH-300) calcined at 300 °C were measured as 1.39 eV and 1.48 eV, respectively. According to the FESEM results, addition of Zn content to the structure of cobalt oxide caused an increase in the E_g due to the smaller particle size in the presence of Zn content.

3.4. FESEM, EDS, and Maps Analysis of the CH and ZCH Samples

FESEM was used to study the morphology of the nanoparticles. FESEM photographs show the pure (Figure 7a,b) and doped (ZCH) samples (Figure 7c,d). Differences in the particle morphology were apparently observed followed by addition of Zn. According to the observations of the cobalt oxide morphology, the particles are irregular in shape; however, this observation is not true about the doped sample. Accordingly, it can be concluded that addition of Zn content increased the porosity and improved the particle morphology. The particle size in the pure cobalt oxide sample is in the range of 20-40 nm, and in the range of about 20-30 nm and in the doped sample whose morphology is quite porous. The average particle size of the calcined ZCH sample at 300 °C is smaller than that of the pure sample

due to the presence of the Zn content. The average particle size of the ZCH sample calcined at 300 °C is about 25 nm. The presence and distribution of elements in the ZCH (Figure 7e) sample calcined at 300 °C were analyzed using Energy Dispersive X-ray Spectroscopy (EDS). The EDS analysis confirmed the presence of cobalt, oxygen, and zinc in the synthesized ZCH sample.

According to the EDS mapping images illustrated in Figure 8, Cobalt (Figure 8a), oxygen (Figure 8b), and zinc (Figure 8c) are homogeneously distributed throughout the region. In particular, Zn is evenly distributed in the surface layers of cobalt oxide nanoparticles.

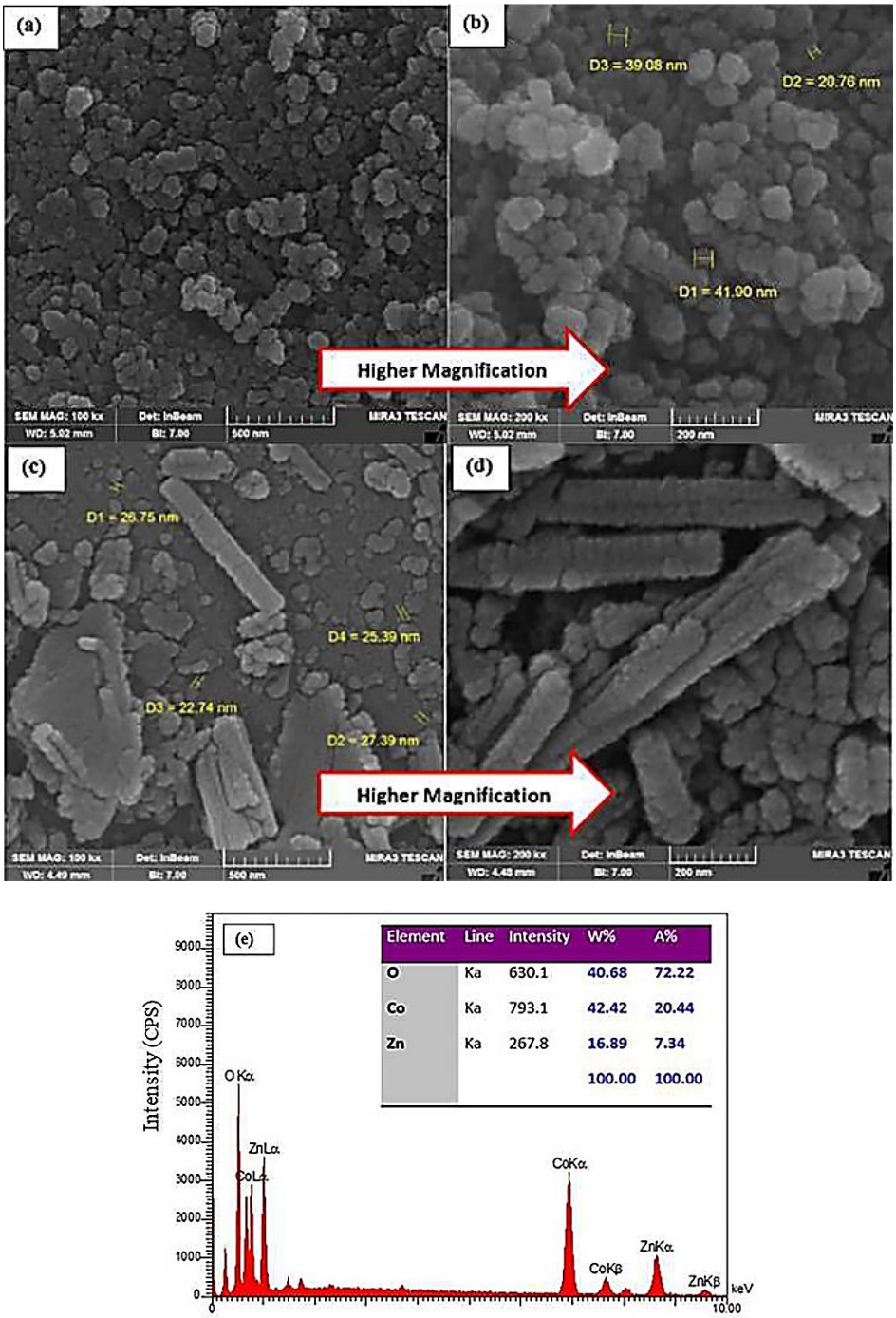

Figure 7. FESEM images of the as-prepared (a, b) Co_3O_4 nanoparticles (CH) and (c, d) ZCH samples at two magnifications, (e) EDS of ZCH-300 (10 % Zn)

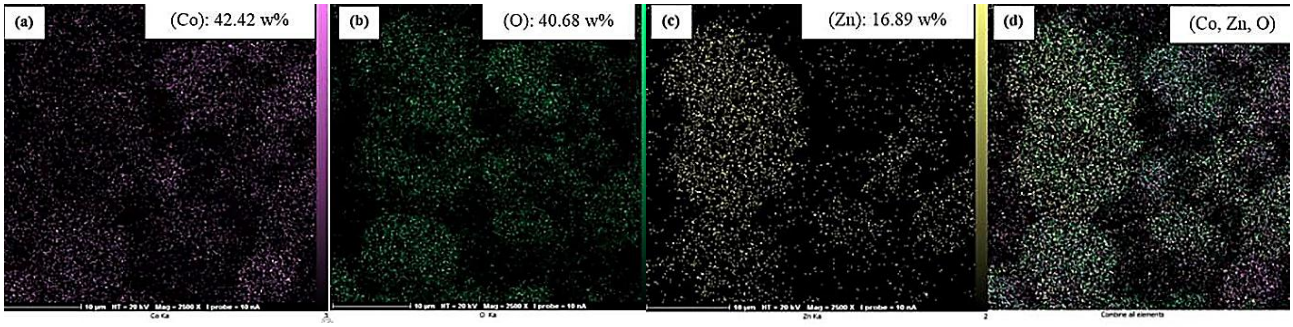

Figure 8. Map distribution of elements at ZCH-300: (a) Cobalt, (b) Oxygen, (c) Zinc, and (d) combine all elements

3.5 TEM Results

The TEM (inset: SAED) pattern depicted in Figure 9a consists of concentric rings, which correspond to (220), (311), and (400) planes of Co_3O_4 with cubic structure. Pure Co_3O_4 nanoparticles (CH) with higher magnification are shown in Figure 9b. According to this figure, the size of the nanoparticles is in the range of 20-30 nanometers. The TEM of the Zn doped Co_3O_4 nanoparticles (ZCH) is shown in Figure 9c. The particle size of the ZCH is in the range of 10-20 nm. Further, HRTEM of Co_3O_4 sample is shown in Figure 9d. In this figure, the distance between the layers (interlayer spacing) is about 0.24 nm and 0.28 nm, which corresponds to the planes with the Miller index (311) and (220) of the cube cobalt oxide structure, respectively.

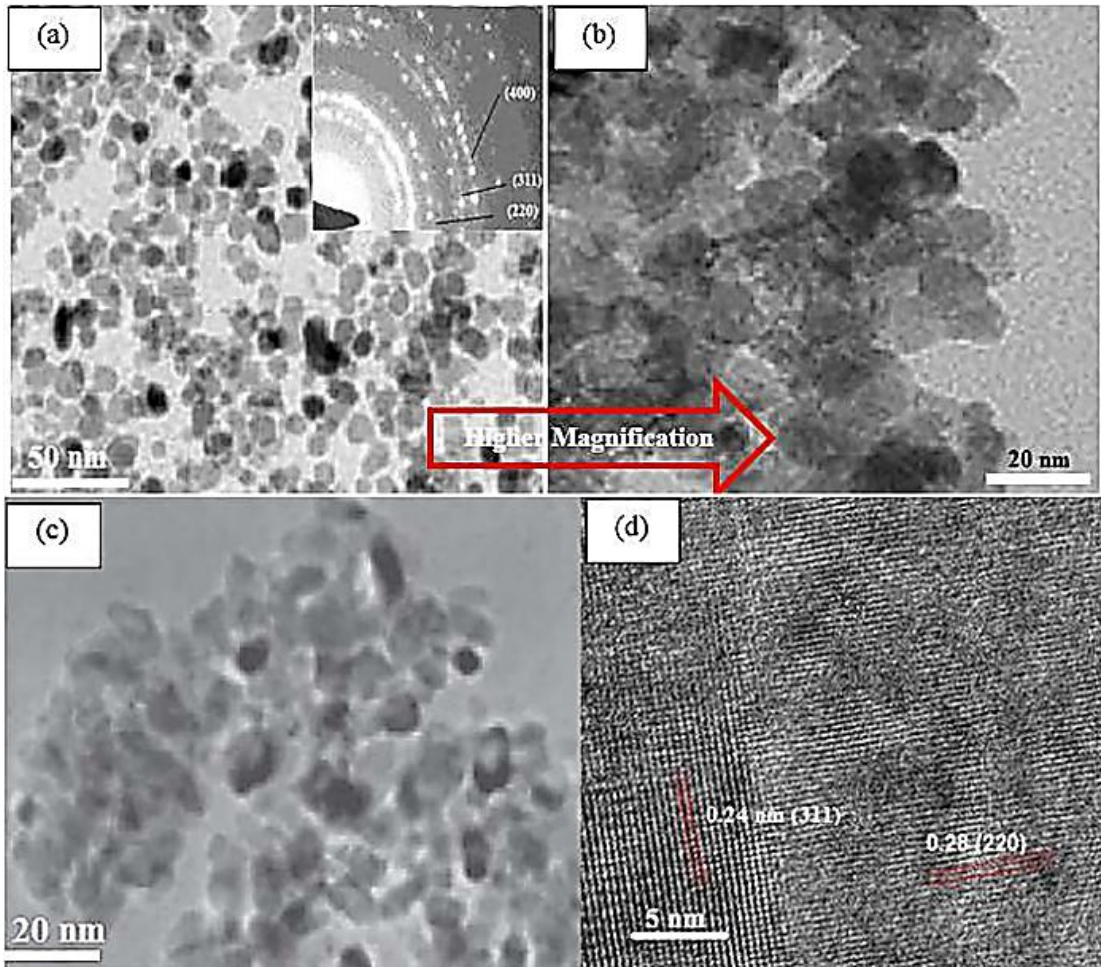

Figure 9. TEM image: (a,b) pure Co_3O_4, (c): Zn doped Co_3O_4(d) HRTEM of Co_3O_4 nanoparticles

4. CONCLUSIONS

In this research, cobalt oxide nanoparticles doped with Zn cations were synthesized by hydrothermal method. The effects of metal ion doping on the crystallizations of Co_3O_4 phase, crystallite size, and optical properties of CH mesoporous nanoparticles were investigated, and the following results were obtained.

- Addition of Zn content to the structure of Co_3O_4 nanoparticles reduced the crystalline size of samples.
- Addition of Zn content to the structure of cobalt oxide at the calcination temperature of 300 ºC led to an increase in the energy of the band gap from 1.39 eV to 1.48 eV mainly due to the smaller size of the particles in the presence of the Zn content.
- According to the FESEM images, the particle size of the pure sample was in the range of 20-40 nm and followed by addition of Zn content to the structure of pure cobalt oxide, the particle size (20-30 nm) decreased. In general, based on the obtained results, ZCH nanoparticles exhibited the best photocatalytical performance owing to a decrease in the electron-hole recombination rate and an increasing in the visible-light capturing.

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Original Research Article

Evaluation of Industrial Policies on the Boom of Domestic Production of Advanced Ceramics Based on an Approach to Environmental Protection

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ABSTRACT

Each year, production of ceramic materials causes many environmental repercussions including air and soil pollution. In addition, due to their nature, industrial environments are susceptible to serious damages and risks that can be potentially exacerbated with the increasing growth of technology. In this regard, the current study aims to evaluate the policies on the prosperity of the domestic production of advanced ceramics with the approach to environmental protection. The current research is among the mixed and exploratory researches that was carried out in two qualitative and quantitative stages. The statistical population includes the senior and executive managers of the "advanced ceramics production industries" in the Ministry of Industry, Mining, and Trade, Iran. This study used the document review tools and semi-structured interviews with 14 academic and executive experts in this industrial field. Based on the "theme analysis" method in this research, the results and consequences of industrial policy assessment were extracted according to the environmental protection approach and finally, these policies were evaluated. The results of this evaluation showed that although some of the production processes of ceramic materials have been modified based on the environmental policies, some other processes are still inconsistent with environmental policies and requirements; therefore, the extent of pollutants in the industrial processes is not accurately monitored and measured, and the level of pollutants in most industrial places is more than the standard level.

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1. INTRODUCTION

The world has been witnessing the emergence and advancement of various forms of changing technologies including information technology, biotechnology, energy, and advanced materials, to name a few. The technologies are expected to have a tremendous economic impact by 2025. Such technologies have four general characteristics in common namely their rapid rate of change, wide area of impact, significant impact on the economic value at a high level, and considerable potential to economic impacts as a projector [1]. One of these technologies is advanced ceramic materials. Advanced ceramics have been included in the list of

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highly important and strategic components in many industries owing to their properties such as stability at high temperatures, high strength and resistance to corrosion, and unique magnetic and electrical properties such as piezoelectricity, superconductivity, insulation or semi-conductivity, etc. In the last 60 years, extensive research has been conducted on 25 different groups of advanced ceramics, which facilitated their vast productions. In recent years, the flourish and expansion of the electronics industry as well as the broad application of advanced ceramics in medical technologies and automobile manufacturing industries has led to the significant growth of the advanced ceramics market and now, these ceramics account for about 50 billion dollars share in the market. In short, since the beginning of the 21st century, some areas such as photonics, biological sciences, and material technology have been assumed to be the most important areas of scientific and industrial progress, and ceramics has been playing a strategic role in all these areas since then. In Iran, like many other parts of the world, a great deal of attention has been paid to these new fields and applications of ceramics and new materials in recent years.

In non-metallic industries, production and progress of tiles and ceramics have caused many environmental problems including air and soil pollution as well as waste production. It goes without saying that the industrial environments are exposed to serious damages that can be potentially intensified and expanded with the increasing growth of technological advancements [2].

For this reason, many international meetings were held in the last years to prevent further environmental destructions in the global scale, and the Islamic Republic of Iran has participated in many of these meetings. It is also committed to taking effective measures in line with the objectives stated in this convention to comply with the environmental requirements [3]. In this regard, more attention has been significantly paid to the evaluation of green industrial policies in recent decades. Governments around the world have intensified their efforts to institutionalize the evaluation of these policies for more efficient, effective, and democratic decision-making [4]. Given the implementation of industrial policies on the boom of production in recent years, it is necessary to make a detailed evaluation of these policies to determine to what extent these policies have been in line with the environmental policies and also to what extent the results of the implementation of these policies could meet the expectations in the field of environment.

2. INDUSTRIAL POLICIES WITH AN ENVIRONMENTAL APPROACH

Industrial policy is about anticipating long-term trends in technology and market development and providing incentives to adapt the structure of the national economy in a way that can take advantage of changes. As climate change and other environmental challenges increasingly affect the future direction of economic development, environmental considerations should become a major part of industrial policy [5]. The main objective of environmental policies is the protection and sustainable use of our natural environment. Intentionally or unintentionally, some of these policies cause structural changes. In these cases, green industrial policy is proposed to include any government action aimed at accelerating the structural transformation towards a low-carbon and resource-efficient economy to flourish productivity in economy [6]. In order to create sustainable economic development, the rate of resource productivity should increase at least with the same amount of economic production. For this purpose, many commercial leaps are technologically possible such as switching to renewable energy, using smart and communication systems, implementing energy-saving technologies, and considering the changes in consumers' behavior. However, to accelerate the required technological and business model innovations, the economic incentives must be very different. Above all, environmental costs should be much better reflected in prices, regulations should be tightened, and subsidies for fossil fuels and other unsustainable products and practices should be reduced. Of note, the global economy is on an unstable path. To be specific, since the Industrial Revolution, the global economy has grown at the expense of destroying the environment. Natural resources have been exploited without permission, pollutants have been accumulated in the biosphere, ecosystems have been severely degraded, and biodiversity has been lost at an alarming rate. Already in the early 2000s, the Millennium Ecosystem Assessment, an UN-led global assessment of the Earth's ecosystems, concluded that about 60 % of ecosystem services have been exploited or used in unsustainable manners.

3. ADVANCED CERAMICS

The term "advanced ceramics" was first coined in the 1970s to designate a new category of engineering materials to introduce new technologies into the 21st century. Since then, there has been phenomenal growth in the technological advancement of these materials. A report from Research and Markets projected the advanced ceramics market to reach US$ 10.4 billion by 2021, growing at a Compounded Annual Growth Rate (CAGR) of 6.5 % [7]. Advanced ceramics are considered integral parts of modern technology. Most of these products perform crucial functions behind the scenes in a number of applications in everyday life. They usually exhibit admirable performance that cannot be easily replicated by other materials [8]. Advanced ceramics today play a key role in technologies such as energy and

environment, transport, life sciences, and communication and information technology [9].

Advanced ceramics exhibit phenomenal performance under severe conditions in a number of areas, including transport, energy and environment, health, high-temperature, electronic, and wear-related applications. However, they have yet to attain the long-expected broad market penetration, especially on the African continent. To be specific, the growth of advanced ceramics usage has been hindered mainly due to the low reliability, brittleness, unfamiliarity to potential users, redesign requirements, and high cost of components. Research and development have led to significant improvements in the properties of advanced ceramics. The past few decades have witnessed the emergence of newer technologies which demand more advanced and higher performance engineering materials in a wide range of applications. Advanced ceramic materials have surpassed a majority of their traditional engineering counterparts and remained uncontested in a wide range of applications. The phenomenal growth experienced is testimony to this. This has been driven mainly by the Asian markets, especially China and Japan [10].

In the last few decades, rapid development in modern communication devices such as cellular telephones, antennae, and global positioning systems has encouraged more thorough research in microwave dielectric materials. Dielectric ceramics are widely used in advanced electronic devices such as capacitors and microwave resonators. They are classified into two broad groups based on their dielectric properties. High quality factor materials are characterized by linear changes in polarization with applied electric field [11].

Thermoelectric (TE) ceramic materials can directly convert heat energy into electrical energy due to the TE effects. A majority of TE devices operating at approximately room temperature are based on bismuth telluride (Bi_2Te_3) and its alloys [12].

The ceramic industry, like all other resources that deal with the transfer and processing of raw materials, has a great impact on the surrounding environment. In fact, a ceramic factory is an open system that receives raw materials, water, fuel, and electricity from the environment, processes and exhaust gases, and produces solid and liquid sewage waste, thermal energy, and smoke.

It should be noted that a ceramic factory has less pollution than many other sources because a significant part of the pollutants created in this industry, especially the solid particles, can be effectively separated at low costs from its entry into the atmosphere. However, the resulting problems should not be underestimated, especially when many factories are concentrated in one area. Fortunately, as a result of preventive measures and awareness, pollutants have been greatly reduced in recent years. Technological advances are one of the important reasons for this pollution reduction [13].

4. RESEARCH METHODLOGY

In this research, the contents of the policies and laws concerning the environmental priorities were examined as follows:

- Article 50 of the Constitution of the Islamic Republic of Iran.
- Economic and other activities that are associated with environmental pollution or irreparable destruction are prohibited.
- Clause 8-1 of General environmental policies (communicated by the Supreme Leader on 8/26/1394).

1-8- Low carbon industry, use of clean energy, healthy and organic agricultural products, and management of wastes and effluents should be prioritized by taking advantage of economic, social, natural, and environmental capabilities.

Followed by interviewing with 14 experts in this field, the basic concepts were extracted, and a thematic analysis method was employed to analyze the data. The interviewees were selected purposefully based on the snowball method. In this method, each expert introduces another expert, and the interview continues until the desired theoretical saturation is reached. During this process, those experts who had the necessary criteria were selected. These criteria were practical experience (i.e., executive experience in the field of industrial policy, especially in production), related field of study (management or engineering field concerning the Ceramics production industry), higher education (master's degree or doctorate), and acquaintance with the field of industrial policies. The characteristics of the mentioned interviewees are briefly listed in Table 1.

TABLE 1. Characteristics of the interviewees

Interviewees	Characteristics	Number
University professors	Faculty Members of the university-PhD Students in the fields of Management (preferably policy orientation) and Non-metallic Materials	5
Representative of the Islamic Council	Representative of the 10th term of the parliament and member of the 6th development plan compilation commission	1
Excellent managers	Managers of Ceramics production industries	2
Managers and senior experts	Relevant people working in developing production promotion policies-managers of Ceramics production industries	6

In the current research, according to the saturation approach, 14 experts were selected as the sample group. After interviewing 11 experts, the answers of the next

experts became similar to those of the previous ones, and the content became repetitive until after the interview with the 13th expert, his knowledge reached theoretical saturation. However, in order to enhance the data practicality, the interviews continued until the 14th experience. Due to the qualitative nature of the theme analysis method, quantitative criteria and positivist approach were not used to control the validity and reliability of the present study; rather, as stated by Guba and Lincoln, the criteria of believability, reliability, verifiability, and transferability [14] were taken into consideration. Here, the following four procedures are used: doing the self-coding test [15], using independent coders, receiving feedback from the interviewees while providing a rich description, and recording the details of the investigations.

5. DATA ANALYSIS AND FINDINGS

By conducting the theme analysis, 172 primary concepts were extracted in the first step. In the next step, after coding the texts, 18 descriptive codes (basic theme) were finally extracted by combining the identified codes based on the degree of conceptual similarity. After analyzing the codes, 10 interpretive codes (organizing theme) were obtained and finally, two relational codes (overarching theme) were obtained through the final review. In order to validate the results based on the Delphi technique as well as the definition of the subject and required expertise, the members of the Delphi panel were selected in three stages through the judgmental non-random sampling method. The first round was done after extracting the primary components from theoretical texts and creating a semi-standard questionnaire. The questionnaire was designed containing two relational codes, five interpretive codes, and 15 descriptive codes. The respondents were asked to answer the question "How effective is each of the dimensions, components, and indicators in the model for evaluating the effectiveness of industrial policies related to production boom?". A five-point Likert scale was used to measure them. After completing and collecting the distributed questionnaires, the results of the first stage were analyzed. According to the opinions of the first round of the panel, three interpretative codes and four descriptive codes that had lower-than-mean agreement and importance were discarded and removed, and no new indigenous codes were added to the experts' suggestion. In the second round, Delphi, once the factors that did not reach consensus in the previous stage were removed, the questionnaire was given to the panel members again. The Kendall coefficient for the second stage questionnaire was 0.653 with the significance level of 0.05. In the third round, the questionnaire was again provided to the panel members. The Kendall coefficient for the third-stage questionnaire was 0.731 with the significance level of 0.05. According to Schmidt, the degree of consensus and unanimity of the members in the second stage, compared to the third stage, increased up to 0.078, and the growth rate of two consecutive periods is quite high. In addition, since the number of panel members is more than 5, a very small amount of W is considered significant; therefore, the repetition of Delphi courses was stopped. After collecting the experts' opinions and adding/subtracting some codes (with the Delphi method), two relational codes, five interpretive codes, and 15 descriptive codes were finally obtained and listed in Table 2.

TABLE 2. Descriptive, interpretive, and relational codes extracted from the present research (researcher-made)

Descriptive Codes	Interpretation Codes	Relational Codes
Development of green spaces to the extent of the development of industrial places Green space maintenance and its effectiveness	Development of green space	Management of natural resources and green space
Use of clean energy Preventing environmentally destructive activities Encouraging environmentally friendly technologies Crimes for entities and persons who violate environmental affairs	Environmental Protection	
Installation of notification and fire extinguishing in industrial places Modifying production processes based on environmental policies Management and control of hazardous and flammable materials and explosions	Compliance with environmental requirements and standards	
Monitoring and controlling the extent of pollutants in industrial processes Air pollutants are under control Reducing the production of industrial pollutants Cleaning up the industrial pollutants	Industrial pollutants	Management of waste and pollutants
Separation of industrial wastes and determination of their duties Management and engineering measures to reduce waste	Effluent and industrial waste	

In order to measure the effectiveness of industrial policies based on environmental protection, it is necessary to check whether a valuable result has been obtained by implementing these policies [16]. Therefore, a survey was conducted with 200 managers, experts, and specialists related to the industry through a questionnaire.

It should be mentioned that it is possible to use the statistical indicators provided by the Statistics Center of Iran, the Central Bank of the Islamic Republic of Iran, and the Strategic Research Center of Expediency Council to directly evaluate the effectiveness of these policies. Nevertheless, there are doubts raised by the scientific community about these data and also some statistical indicators are calculated using artificial methods which lead to different results [16]. Therefore, to evaluate the effectiveness of these policies, the mentioned method was used. The results of this test will be discussed below. To implement statistical methods and calculate appropriate test statistics and logical inferences about research hypotheses; the most important action is to choose the appropriate statistical method for the research before any action. For this purpose, knowledge of data distribution has a basic priority. In this research, the Kolmogorov-Smirnov test was used to check the assumption of normality of the research data. The result of this test is shown in Table 3. Because the sig obtained for all variables is greater than 0.05, it can be concluded that the research hypothesis is rejected and the null hypothesis is confirmed, as a result, the data distribution of all variables is normal.

As shown in Table 3, in all cases, a significance value greater than 0.05 was obtained. Therefore, there is no justification to reject the null hypothesis based on the normality of the data. In other words, the distribution of the research data is normal; hence, the parametric tests can be done.

TABLE 3. Calculation of the Kolmogorov-Smirnov test

Components	**Number**	**Normal parameters**		**The maximum amount of differences**			**The value of the test statistic**	**The significance level of Sig**	**Test result** (normal distribution)
		Mean	Standard Deviation	Absolute	Positive	Negative			
Effluent and industrial waste	200	3.1250	1.31071	0.178	0.113	-0.178	1.178	0.445	✓
Industrial pollutants	200	3.1888	0.61875	0.143	0.086	-0.143	1.143	0.224	✓
Management of waste and pollutants	200	3.0375	0.90495	0.175	0.110	-0.175	1.175	0.125	✓
Development of green space	200	3.0683	0.78604	0.142	0.080	-0.142	1.142	0.127	✓
Environmental Protection	200	3.2183	0.69744	0.122	0.095	-0.122	1.122	0.075	✓
Compliance with environmental requirements and standards	200	3.1600	0.90332	0.147	0.088	-0.147	1.147	0.122	✓
Management of natural resources and green space	200	3.1255	0.46872	0.100	0.076	-0.100	1.100	0.113	✓

6. INVESTIGATING THE EFFECTIVENESS OF INDUSTRIAL POLICIES WITH THE APPROACH TO ENVIRONMENTAL PROTECTION

To measure the effectiveness of these policies, 14 interview questions were designed, considering the indicators identified for the indicators related to the research topic, in the form of a questionnaire in a five-point scale and then, the questionnaires were given to 200 experts in this field. Next, the collected data was evaluated using a one-group t-test. Table 4 also shows the results of the one-sample t-test to examine the current status of indicators for evaluating the effectiveness of industrial policies with the approach of environmental protection.

According to the questionnaire scale, which was a five-point Likert one, the basis of the decision was considered on a score of 3. As Table 5 shows, regarding natural resources and green space management indicators, the t statistic calculated 3.816, 3.110, and 2.514 in the indicators "with the implementation of industrial policies, green space has been developed to the extent of the development of industrial places", "with the implementation of industrial policies, there is a written program for the maintenance of green spaces and their effectiveness", and "using environmentally-friendly fuel materials is promoted by implementing industrial policies", respectively, which is significant at the 0.05 level. A comparison of the mean of the dimensions (3.1600), (3.2650), and (3.2050) with the expected mean (score 3) shows that these three components are valid from the experts' viewpoint and confirmed with 95 % confidence.

In relation to other indicators of natural resources and green space management, the t statistics calculated for the indicators "environmentally destructive activities are prevented by the implementation of industrial policies", "environmentally-friendly technologies are encouraged and promoted by the implementation of industrial policies", "with the implementation of industrial policies, crimes are attributed to units and persons who violate environmental affairs", "with the implementation of

TABLE 4. The results of the one-sample t-test considered to examine the current status of the indicators used for evaluating the effectiveness of industrial policies with the approach to environmental protection

Components	Expected Mean=3						
	T	Degree of Freedom	Significance Level	Mean	Mean Difference	95 % Confidence Interval Meaning of Differences	
						Lower Limit	Upper limit
With the implementation of industrial policies, green space was developed to the extent of the development of industrial places	3.816	199	0.041	3.1600	0.16000	-0.0137	0.3337
With the implementation of industrial policies, there is a written program for the maintenance of green spaces and their effectiveness	3.110	199	0.002	3.2650	0.26500	0.0970	0.4330
Using environmentally friendly fuel materials is promoted by implementing industrial policies	2.514	199	0.013	3.2050	0.20500	0.0442	0.3658
Environmentally destructive activities are prevented by the implementation of industrial policies	1.349	199	0.179	3.1250	0.12500	-0.0578	0.3078
Environmentally friendly technologies are encouraged and promoted by the implementation of industrial policies	0.169	199	0.866	3.0150	0.01500	-0.1604	0.1904
With the implementation of industrial policies, crimes are determined for units and persons who violate environmental affairs	0.650	199	0.517	3.0600	0.06000	-0.1221	0.2421
With the implementation of industrial policies, fire alarms and extinguishing systems have been installed in industrial places	0.997	199	0.320	3.0900	0.09000	-0.0880	0.2680
With the implementation of industrial policies, dangerous and hazardous substances ignition, and explosion are under control	1.576	199	0.117	3.1400	0.14000	-0.0352	0.3152
With the implementation of industrial policies, the production processes have been modified based on environmental policies	-0.274	199	0.784	2.9750	-0.02500	-0.2048	0.1548
With the implementation of industrial policies, the extent of pollutants in industrial processes is monitored and measured	2.009	199	0.046	3.1800	0.18000	0.0033	0.3567
With the implementation of industrial policies of air pollutants in places industrial is measured	2.769	199	0.006	3.2250	0.22500	0.0647	0.3853
With the implementation of industrial policies, the production of industrial pollutants has decreased	2.790	199	0.006	3.2500	0.25000	0.0733	0.4267
With the implementation of industrial policies, industrial wastes are separated and assignments are determined	2.970	199	0.003	3.2650	0.26500	0.0890	0.4410
With the implementation of industrial policies, managerial and engineering measures are taken to reduce waste	0.586	199	0.558	3.0550	0.05500	-0.1300	0.2400

industrial policies, fire alarms and extinguishing systems have been installed in industrial places", "with the implementation of industrial policies, dangerous and hazardous substances ignition, and explosion are under control", and "with the implementation of industrial policies, the production processes have been modified based on the proposed environmental policies" were not significant at the 0.05 level, and their mean was not different from the expected mean (score 3). According to the experts, these indicators have had a moderate impact on the effectiveness of industrial policies with an environmental protection approach. In the indicators of waste and pollutants management, the t statistics were calculated 3.1800 for "with the implementation of industrial policies, the extent of pollutants in industrial processes are monitored and measured", 3.2250 for "with the implementation of industrial policies of air pollutants in places industrial is measured", 3.2500 for "with the implementation of industrial policies, the production of industrial pollutants has decreased", 3.2650 for "with the implementation of industrial policies, industrial wastes are separated and assignments are determined", and 3.0550 for "with the implementation of industrial policies, managerial and engineering measures are taken to reduce waste", which were significant at the 0.05 level with their mean higher than the expected mean (score 3).

Therefore, according to the experts, they have had a great impact on the effectiveness of the industrial policies with the approach of protecting the environment.

Table 5 shows the results from the evaluation of the components of the effectiveness of industrial policies with the environmental protection approach. According to the results of the one-sample t-test (Figure 1) and exploratory factor analysis, the current situation is as follows: the components of sewage and industrial waste with the value of t = 3.567, environmental protection t = 4.427, and compliance with the environmental requirements and standards t = 2.505 are significant at the 5 % error level (P < 0.05). Therefore, the null hypothesis that there is no difference between the observed mean and community mean (3) is rejected, and it is concluded that there is a significant difference between the observed mean and community mean (3). Therefore, the components of "effluent and industrial waste", "environmental protection", and "compliance with environmental requirements and standards" were approved by experts with 95 % certainty. However, in the components of "industrial pollutants" and "development of green space", a comparison of its mean with the expected mean (score 3) does not show a significant difference that these two components have a moderate level of credibility according to experts.

TABLE 5. One-sample t-test results to check the current status of the research components

Components	Expected Mean=3						
	t	Degree of Freedom	Significance Level	Mean	Mean Difference	95 % Confidence Interval Meaning of Differences	
						Lower Limit	Upper Limit
Effluent and industrial waste	3.567	199	0.000	3.2125	0.21250	0.0950	0.3300
Industrial pollutants	1.349	199	0.179	3.1250	0.12500	-0.0578	0.3078
Management of waste and pollutants	4.314	199	0.000	3.1888	0.18875	0.1025	0.2750
Development of green space	1.229	199	0.220	3.0683	0.06833	-0.0413	0.1779
Environmental Protection	4.427	199	0.000	3.2183	0.21833	0.1211	0.3156
Compliance with environmental requirements and standards	2.505	199	0.013	3.1600	0.16000	0.0340	0.2860
Management of natural resources and green space	3.787	199	0.000	3.1255	0.12550	0.0601	0.1909

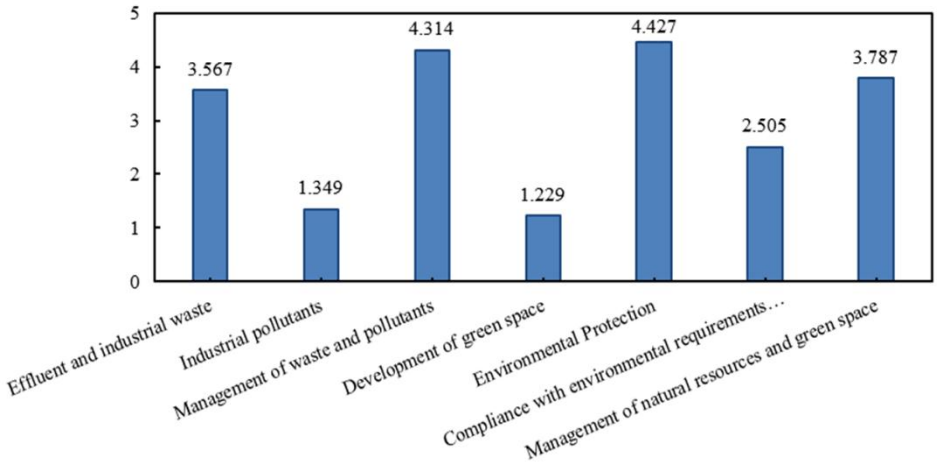

Figure 1. T-test results graph

7. CONCLUSION

According to the evaluation results, in the case of implementing industrial policies in the Ceramics production industries, despite the development of the green space to the extent of considerable increase in the areas of industrial places, proposal of a documented plan for the maintenance of the green spaces and their effectiveness, and extensive use of environmentally-friendly fuel materials, serious crimes have not yet been considered for units and persons who are recognized violators in environmental affairs, hence incapable of deterrent. Although fire alarm and extinguishing system were already installed in some sensitive industrial areas, there are still other vast areas that have not been covered

yet. In addition, some reports denote that some dangerous and flammable materials and explosion are not fully under control and supervision. Although some of the production processes were modified based on environmental policies, there are still a number of processes that are not aligned with environmental policies and requirements. In terms of the pollutants and industrial wastes management, it should be noted that the production level of pollutants in industrial processes is not accurately monitored and measured, and the amount of pollutants caused by industrial production has threateningly increased in some cases. Moreover, industrial production wastes are not completely planned, segregated, and determined. In short, although some measures are currently being taken to reduce the amounts of waste and effluents from industrial production, these measures are not effective enough, hence the need for further considerations.

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Original Research Article

Investigating the Process of Producing Scientific Clinical Research about Zirconia Implants: A Bibliometric Visual Mapping Approach

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ABSTRACT

Nowadays, implants are considered the most suitable alternatives to restoration of lost organs owing to their good mechanical properties and smooth surface, which are similar to those of bone tissue. One of the newest types of implants is zirconia implant, which reduces the possibility of infection due to its one-piece design. Zirconia implants proved to be biocompatible and less prone to corrosion than their traditional titanium counterparts, making them a beneficial option for dental implantation. Another reason why zirconia implants are superior to titanium ones is their better compatibility with soft tissues and greater durability against pressure and tension. Zirconia implants generate less stimulation of the soft tissues, hence lower levels of irritation and inflammation. As a result, zirconia implants are less likely to cause irritation or inflammation. In this research, articles published within the time period of 1980-2022 were examined and processed using VOSviewer software. The total number of articles examined was 3122, 47.6 % of which were published within the last five years. The results revealed that a majority of the articles were from America and Germany. India had the highest Compound Annual Growth Rate (CAGR) of 40 %, followed by Brazil and Spain with the CAGRs of 28 % and 25 %, respectively. Moreover, developing countries such as Poland, Taiwan, Iran, and Egypt have recently started their research activities in this field.

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1. INTRODUCTION

In numerous clinical cases such as dentistry and bone repair, there is a requirement to produce and reconstruct bone which would be best accomplished through spontaneous bone growth and repair. However, in most cases, the tissue cannot be transformed into the shape needed for successful bone regeneration. Therefore, the focus has been shifted to the application of implants [1].

One of the modern sciences that has made significant progress in recent years and has been able to reduce human concerns about tooth loss to a great extent is dental implantation. Despite the wide applications of titanium implants technology in this field. The prolonged stabilization period required for this type of implant and two-stage implantation procedure which takes a considerable duration of time (3-6 months) to create an integrated space with the bone can result in bone resorption. From a surgical perspective, implanting this type of implant in cases where the jaw bone is atrophied is also quite difficult [2-4].

Recently, use of zirconia implants has been highly

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recommended due to their biological compatibility with the bone tissues as well as their one-stage implantation process [5]. In addition, zirconia implants have high resistance that enables them to withstand quite high pressures. One of the main reasons behind the popularity of zirconia implants is their high durability and strength. In addition, due to the one-piece design of the zirconia implants, the possibility of infection and further problems related to the connection of the abutment to the implant is significantly reduced. In the two-piece designs that are commonly found in titanium implants, there is a possibility of bacteria infiltration and accumulation at the connection site of the abutment to the implant which in turn increases the risk of infection. Additionally, there is a possibility of abutment loosening due to severe jaw pressure, a problem that is resolved with the one-piece design of zirconia implants [6,7].

Zirconia is a crystalline form of an intermediate metal called zirconium, and zirconia implants are often known as metal-free implants [8]. Due to the increasing concerns about the presence of mercury in titanium implants, patients prefer to use metal-free implants. Research has shown that ceramic zirconia implants easily integrate with the bone, hence no signs of inflammation [9-11]. Other researchers also reported that zirconium is an ideal element for use in dental implants [12,13]. Zirconia implants have a very high success rate owing to their biocompatibility. Integration of the bone with this type of implant is quite satisfactory. For this reason, the implant is characterized by the strength similar to that of natural teeth [14].

In addition to the advantages mentioned earlier, it is important to be aware of the fracture potential in zirconia crown prostheses used in artificial teeth. Factors that cause fracture include the design errors, excessive force, surface cracks, and weak tooth foundations. To prevent fracture, it is essential to use appropriate prosthesis materials of high quality and adhere to the standards designated to the design and implementation of zirconia crown prostheses. Additionally, it is critical to evaluate the patient's oral and dental conditions before beginning treatment to identify and address any issues that may increase the risk of fracture. By taking these precautions, dental practitioners can ensure the longevity and effectiveness of zirconia crown prostheses for their patients [15,16].

Zirconia is a highly versatile material that can be used in a variety of dental implant applications. To cater to specific biological and mechanical requirements, different types of zirconia can be utilized for monolithic implants. High-translucent zirconia, for instance, is preferred for anterior teeth, where translucency is crucial for a natural-looking appearance. This type of zirconia offers outstanding optical properties that make it suitable for single-unit implants, implant-supported bridges, and implant-supported dentures. On the contrary, medium-translucent zirconia is best suited for posterior teeth and implant-supported restorations where both strength and durability are of utmost importance. Its good mechanical properties make it ideal for implant-supported bridges and full-arch restorations. When extreme loads are expected (as in bruxism or clenching cases), high-strength zirconia is preferred. This type of zirconia boasts excellent mechanical properties, including high flexural strength and fracture toughness, making it an ideal choice for implant-supported restorations in high-stress areas. In recent years, bioactive zirconia has emerged as a new type of zirconia that promotes osseointegration and bone regeneration. This type of zirconia is coated with a bioactive material that contributes to bone growth and attachment, making it an excellent choice for cases involving bone loss or regeneration. Overall, selection of zirconia for monolithic implants will depend on a range of factors, including the patient's clinical requirements, aesthetic preferences, and mechanical demands for restoration. By carefully choosing the right type of zirconia, dental practitioners achieve optimal results and enhance patient outcomes [17-21]. Given the aforementioned points, investigating the achievements and research in the realm of zirconia dental implants gains significance that is carried out through a scientific method known as scientometric.

With the continuous growth and advancement in science, there have been changes in scientific fields, and the scope of these changes is extending day by day. These changes have caused outdated scientific realities to lose their prevalence to the extent that Thomas Kuhn interprets this change and evolution in science and technology as a scientific revolution [22]. One of the areas that have emerged in recent decades as a result of these scientific changes and developments is the field of scientometrics. Simply put, scientometrics is the method for measuring science which includes all quantitative methods and models related to the production and dissemination of knowledge and technology. Scientometrics provides quantitative and comparative evaluations of the knowledge progress among researchers, groups, institutions, and countries and helps gain a better understanding of the construction of scientific research through the analysis of the quantitative aspects of scientific productions and application of such information [22,23].

Nowadays, scientometrics is one of the most common methods for evaluating scientific activities and research management. The rapid development of information in scientometrics, on the one hand, and the changes in this field as a research area, on the other hand, led to its confrontations with huge amount of information [23]. Under such circumstances, tracking subjects, identifying vocabulary and concepts, and understanding the structural relationships between these concepts become challenging. Additionally, scientometric methods have drawn interest in various fields. Given that changes in various scientific fields are inevitable, they also cause

differences in vocabulary, content, and meaning [24]. Therefore, creating a picture of the status of research conducted in this field and drawing a conceptual structure based on co-occurrence analysis as a model are necessary. Co-occurrence analysis is an efficient content analysis method based on the co-occurrence of vocabulary in texts and documents. One of its main applications is to create a network of conceptual documents for better analysis and evaluation of a scientific field [25].

A research was conducted on the scientific trends and clinical research on zirconia dental implants using the Web of Science database. The results of this article show that the number of such studies on the zirconia dental implants have significantly increased in recent years. It can also be concluded that use of zirconia dental implants can be an alternative method to metallic dental implants [26].

With an increase in the number of published articles on the dental implants, more advancements and trends have emerged in vital research areas. In this regard, the main objective of this research is to investigate the progress and trends concerning the applications of zirconia dental implants, identify the leading countries in this regard, and finally predict the future changes in this research field.

2. MATERIALS AND METHODS

Some articles about zirconia implants were found in Scopus from 1980 to 2022 using the following keywords: TITLE-ABS-KEY (zircon) OR TITLE-ABS-KEY (zirconium) OR TITLE-ABS-KEY (zirconia) AND TITLE-ABS-KEY (oral implant) OR TITLE-ABS-KEY (dental implants) OR TITLE-ABS-KEY (dental implant) OR TITLE-ABS-KEY (oral implants) OR TITLE-ABS-KEY (dental implantation) OR TITLE-ABS-KEY (dental implantology) OR TITLE-ABS-KEY (implant dentistry) OR TITLE-ABS-KEY (osseointegrated dental implantation) OR TITLE-ABS-KEY (osseointegrated). The article information, including its year of publication, title, authors, keywords, abstract, and downloaded source affiliations, were processed using the VOSviewer software. This process is illustrated in Figure 1.

3. RESULTS AND DISCUSSION

Figure 2a shows the number of published articles from 1980 to 2022. The total number of published articles was 3122, 79.5 % of which (2483 articles) were published in the past ten years and 47.6 % (1489 articles) in the past five years. The highest number of published articles was in 2022 and 2021, with 351 (11.2 %) and 338 (10.8 %) articles, respectively. Evidently, the trend of articles about the zirconia implants has increased over time, and most of the articles have been published in recent years. Figure 2b shows the top 10 journals with the highest number of publications related to zirconia implants. Journal of Prosthetic Dentistry (6.8 %, n = 213) and Clinical Oral Implants Research (6.5 %, n = 205) had the highest number of published articles. Among the top 10 journals that have published articles about zirconia dental implants, Dental Materials journal with an IF of 5.304 has published 2.2 % of the total articles in this field.

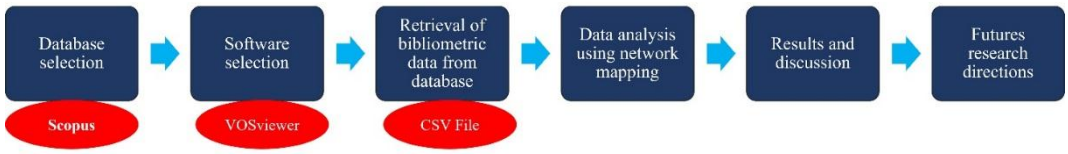

Figure 1. Stages of conducting research

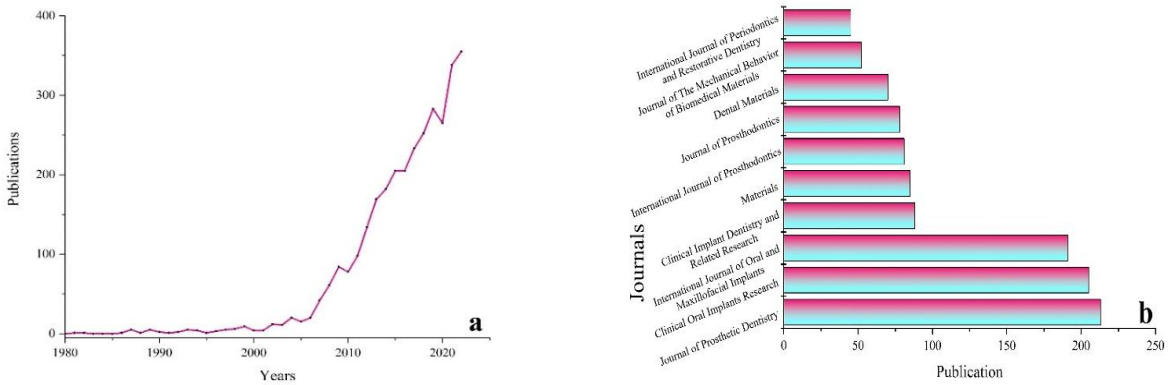

Figure 2. Published articles on zirconia implants: (a) by year of publication, and (b) by publication in journals

Figure 3 shows the annual number of articles on zirconia implants in top 10 countries with the highest number of articles in Scopus database. Initially, Japan had the highest number of articles but over time, the United States and Germany competed closely from 1980 to 2022. In some years, the United States had more articles while in others, Germany surpassed the USA. However, the United States surpassed Germany in 2020 with the highest number of articles about zirconia implants.

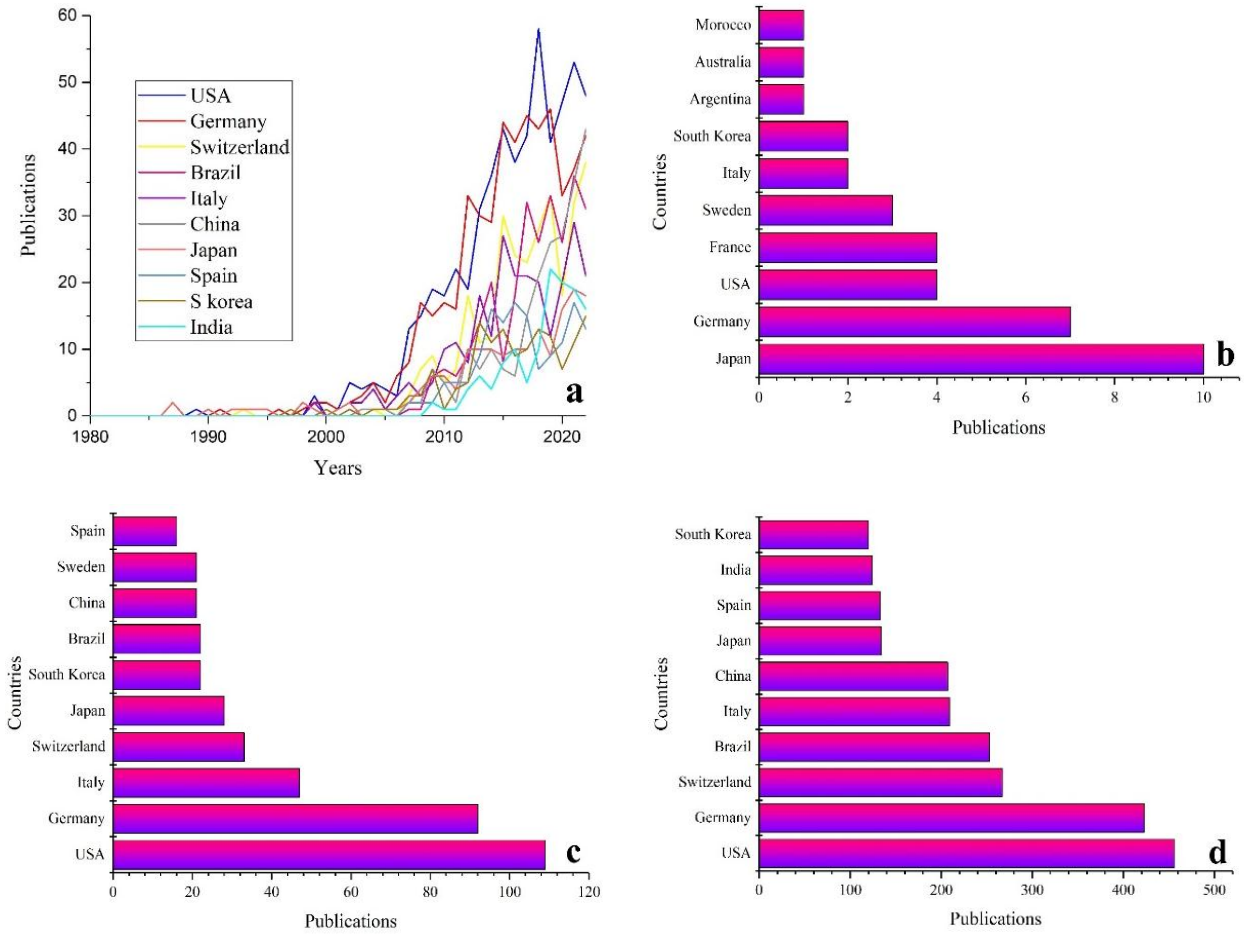

Figure 3. Articles on zirconia implants in the top 10 countries: (a) 1980-2022, (b) 1980-2000, (c) 2001-2011, and (d) 2012-2022

Figure 4 shows Compounded Annual Growth Rate (CAGR) [27,28] from 2010 to 2019 of the top 10 countries in the field of zirconia implants. India had the highest growth rate of over 40 % in the past 10 years. Research on zirconia implants in India began in the early 2009 that was further expanded with the support of the Saveetha Institute of Medical and Technical Sciences and later the Saveetha Dental College and Hospitals.

After India, Brazil, and Spain had the second and third highest growth rates of 28 % and 25 %, respectively, while the United States followed a declining trend with the CAGR of 16 %. In order to examine the relationship between the leading countries in the field of zirconia implants, VOSviewer software and Scopus data were used. Out of a total of 154 countries, 30 countries have 20 or more articles, as shown in Figure 5. The thickness of the lines is indicative the degree of cooperation among

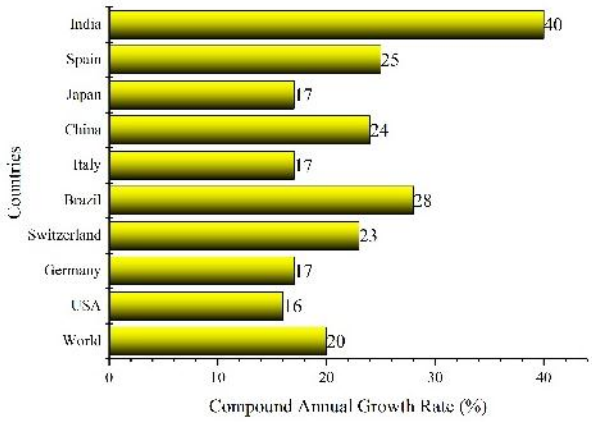

Figure 4. The compounded annual growth rate (CAGR) of the top 10 countries in the field of zirconia implants

the countries, and the size of the circles indicates the number of articles. Additionally, the more yellow the color, the higher the number of articles for that country. As evident, the United States and Germany have more publications and cooperation with each other than other countries. Of note, Poland, Taiwan, Iran, and Egypt have recently started their activities in this field.

Figure 6 depicts a map of the relationships and collaborations among individuals in the field of zirconia implants. The total number of authors was 8,917, 29 of whom have published at least 15 articles. The largest network of connections belongs to "Sailer i" with 14 researchers and "Kohal r.j" and "Spies b.c" with 13 researchers.

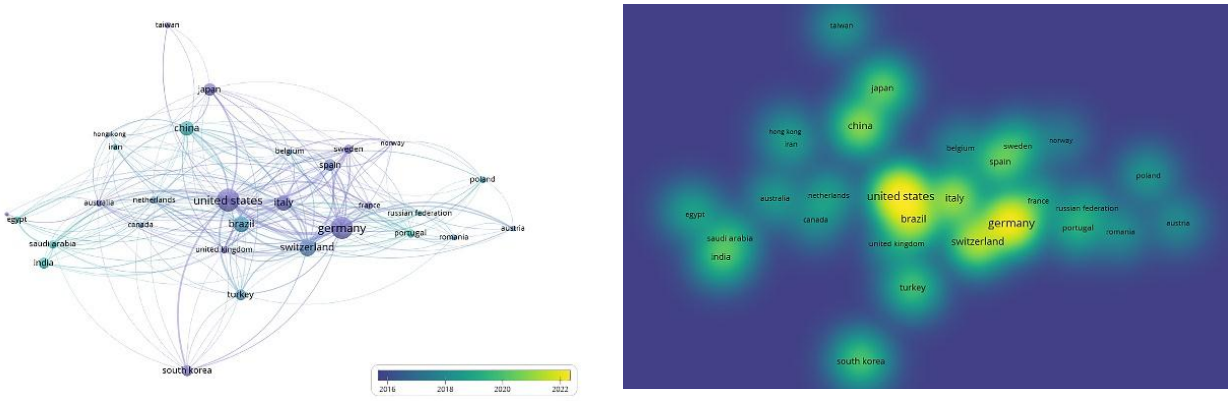

Figure 5. Map of active countries in the field of zirconia implants and their research relationships with each other

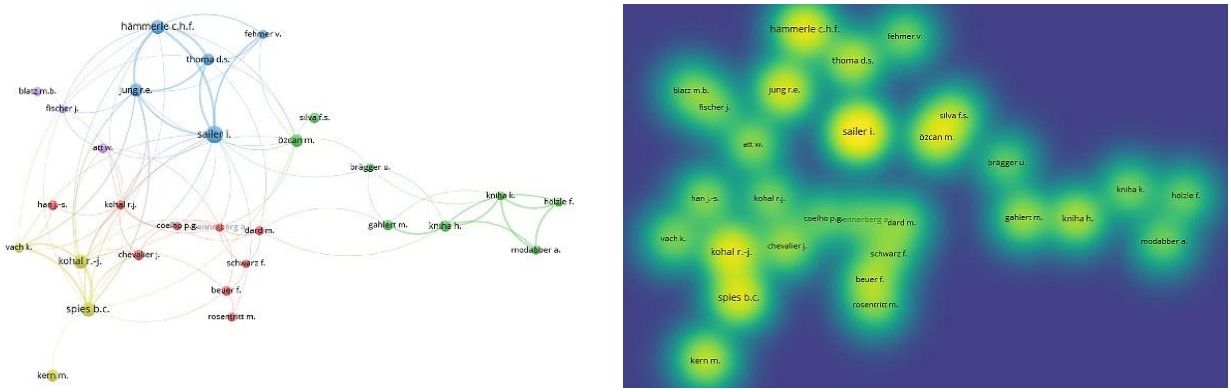

Figure 6. Map of active individuals in the field of zirconia implants and their research collaborations with each other

Figure 7 shows the research trend using words related to zirconia implants. Out of a total of 11,994 words, only 23 words have been repeated at least 500 times. The increase in the distance between two words implies that they are less likely to occur together.

On the contrary, the decrease in the distance between two words shows that they are more likely to occur together, and the size of the circle is indicative of the frequency. According to this figure, the words "Zirconium," "Human," and "Zirconium oxide" have the highest frequency of occurrence.

Figure 8 demonstrates the communication network of authors based on Citation/Document and Citation/Author. As shown in Figure 8a, out of a total of 3122 published articles, only 20 articles about zirconia implants had more than 250 citations, with "Piconi c" having 9 connections and "hisburgues m" having 7 connections with other authors with the highest communication network.

According to Figure 8b, out of a total of 8917 authors, 33 authors had at least 10 published articles in this field with 500 citations. Among them, "kohal r.j" had the highest communication network with 32 connections followed by "hammerle c.h.f" and "junge r.e" with 31 connections with other authors.

Figure 9 shows the active research centers in the field of zirconia implants. As shown, University of Buenos Aires, Hiroshima University, and Pitie-Salpetriere University Hospital were among the first centers to initiate research in this area. From 2001 to 2011, University of Freiburg and University of Zurich were also active. Since 2012, University of Zurich has continued to grow and has taken the lead along with University of Bern, surpassing the other centers.

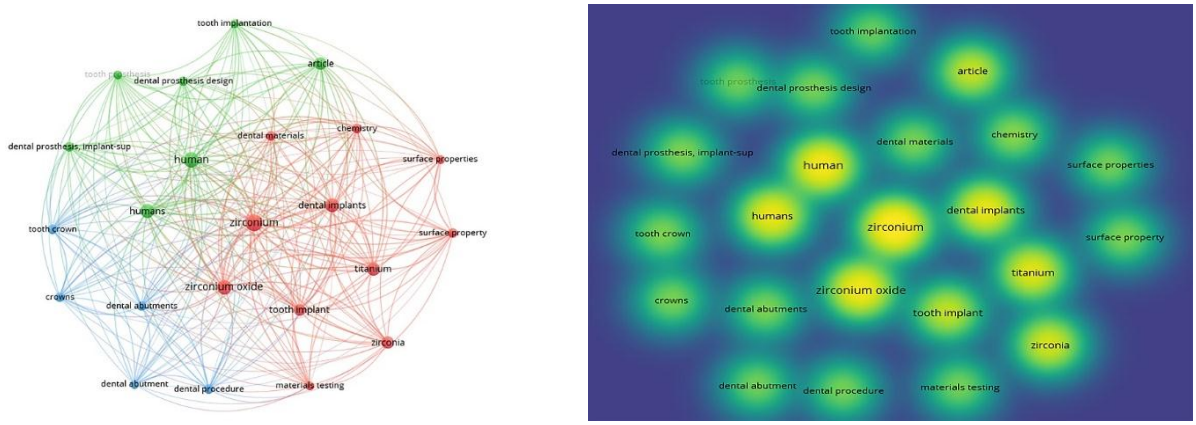

Figure 7. Map of frequently used words in the field of zirconia implants

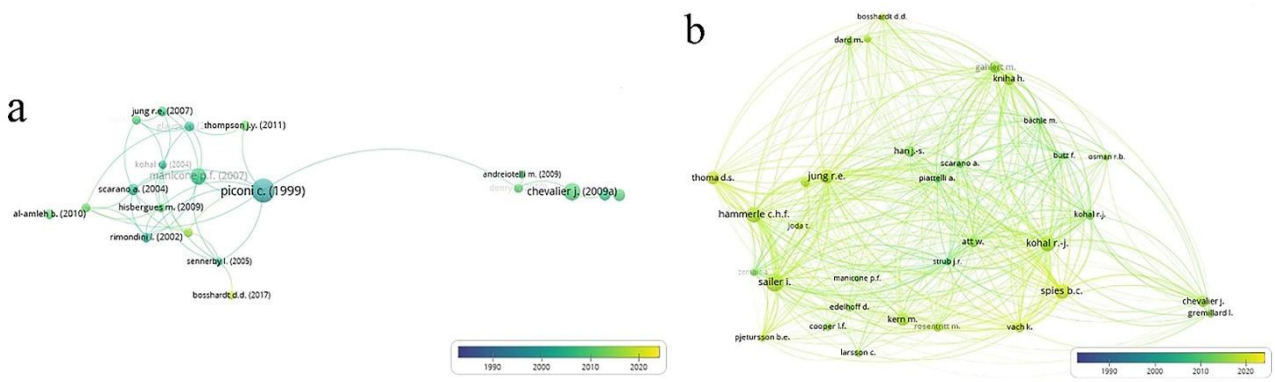

Figure 8. The communication network of authors based on (a) Citation/Document and (b) Citation/Author

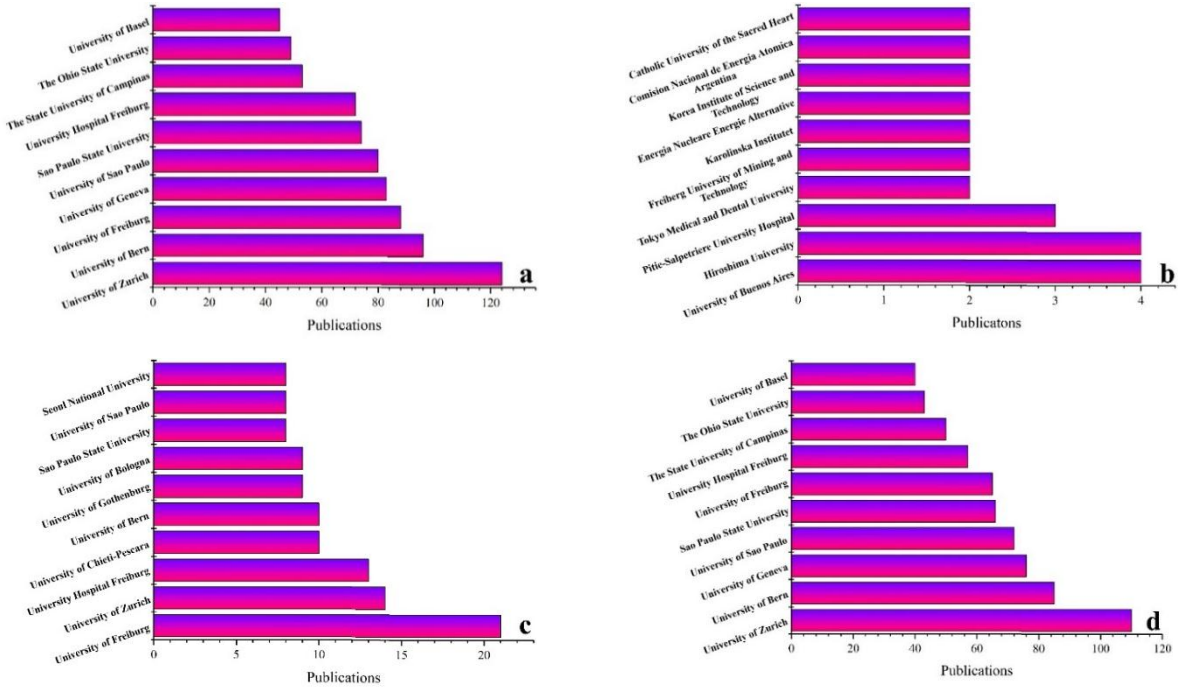

Figure 9. Active research centers in the field of zirconia implants: (a) 1980-2022, (b) 1980-2000, (c) 2001-2011, and (d) 2012-2022

Undoubtedly, future studies on zirconium implants is essential for further advancements in and understanding their potential applications. Conducting long-term clinical studies are also necessary to evaluate the lifespan and effectiveness of zirconium implants. The current research monitored patients over several years and assessed the success rate of their implants. Additionally, further research on the antibacterial properties of zirconium implants can lead to the development of even more effective coatings that reduce the infection risk.

While zirconium implants are generally well-tolerated by the body, further research can help identify the potential biocompatibility issues that may arise in some patients. This research can also ensure the development of more biocompatible materials and designs. In addition, research on the potential of zirconium implants to facilitate bone regeneration paves the way for the scientific creation of implants that strengthen bone restoration and repair, which can be useful in cases of bone loss or severe damage. Since zirconium implants gain increasing popularity due to their aesthetic properties, further research ensures the development of implants with a more natural and durable appearance.

Overall, future research on zirconium implants explores even more effective and versatile implant options that can improve the patient's achievements and life quality.

4. CONCLUSIONS

1. Further exploration in the field of implant innovation is of high importance for the future development of body health. For this reason, more attention has been drawn to zirconia implants over time. Research has shown that from 2000 to 2022, the United States and then Germany were the two leading countries in publishing articles about zirconia implants.
2. India had the highest growth rate in publishing articles with the CAGR of 40 % while the CAGR of the United States was 16 %.
3. Recently, some developing countries including Poland, Taiwan, Iran, and Egypt have started their research activities for further development of zirconia implants.

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