Review: Photocatalytic Geopolymers for Degradation of Cationic and Anionic Dyes in Wastewater Treatment

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**Abstract.** The development of geopolymers for wastewater treatment has increased. Geopolymer photocatalysts have been proven to be an effective and cost-effective solution for water treatment. This review discusses the utilization of geopolimer photocatalysts for degrading two types of dyes, namely anionic and cationic dyes, and makes a simple comparison between them, thus opening the door to a better understanding of the dye degradation process by geopolimer photocatalysts. Both types of dyes are carcinogenic and mutagenic and can pose risks to the environment and human health. Geopolymer photocatalysts are capable of removing both types of dyes with an average degradation efficiency of 96.23% for cationic dyes and 96% for anionic dyes. This efficiency is linked to the presence of negatively charged aluminum in the geopolymer microstructure, which affects dye interaction with the photocatalytic geopolymer membrane. Moreover, the efficiency also depends on factors such as the solution's pH, the initial concentration of dye waste, contact time, photocatalyst dosage, and the type of photocatalyst used. The solution pH is directly related to the dye degradation process as it can affect the surface charge of the geopolymer photocatalyst. Additionally, the photocatalytic agents also influence the degradation percentage due to their varying energy band gaps. Excessively high initial concentrations could obstruct light penetration due to the dye's opacity, thereby hindering the photocatalysis process. Conversely, low concentrations reduced the driving force at the solid-liquid interface, impairing the efficiency of the reaction. Increasing the photocatalyst dosage could enhance degradation efficiency; however, exceeding the optimal concentration threshold might lead to particle agglomeration, thereby reducing photocatalytic efficiency.

# INTRODUCTION

The issue of water pollution was one of the global agendas of the Sustainable Development Goals (SDGs) regarding the resolution of the Clean Water and Sanitation issue, targeted to be fully resolved by 2023. The main cause of water pollution was dye waste [1]. Dyes have been widely used in industries such as textiles, leather, paper, automotive, and printing. It was estimated that one million tons of dyes were produced each year, and about 50,000 tons were directly disposed of during the manufacturing and dyeing processes without treatment [2]. Dyes could be classified into two main categories: cationic dyes and anionic dyes. Both types of dyes had harmful effects on human health and the environment due to their toxic, carcinogenic, mutagenic, non-biodegradable properties, and their ability to block sunlight in water bodies, making it important to treat dye waste before disposal.

Several techniques have been developed for wastewater remediation, including biodegradation methods (fungi, algae, bacteria, and microbial fuel cells), coagulation, photocatalytic oxidation, ozone adsorption, Fenton, and ion exchange [3]. The coagulation process generally produced a by-product in the form of toxic sludge [4]. The adsorption method could not be operated continuously [5]. Meanwhile, the advanced oxidation process had relatively high operational costs [6]. This situation led to the emergence of a new method: selective separation using membranes. Membrane separation was an environmentally friendly wastewater treatment method that had rapidly developed over

two decades. Membranes had long-term stability and were not easily decomposed, either biologically, chemically, or physically [7], [8].

Membrane materials have undergone rapid development over the past decade. Based on raw materials, membranes could be divided into organic membranes and inorganic membranes. Organic membranes had the advantage of a relatively simple manufacturing process and low energy requirements, but they had drawbacks such as instability at high temperatures, extreme pH levels, and decomposition in organic solvents [9]. Conversely, inorganic membranes had good pressure or temperature stability and were highly selective and permeable to specific molecules. However, inorganic membranes faced fabrication challenges due to the need for high temperatures and high costs [10]. Therefore, another potential solution was the use of inexpensive materials that were easy to prepare yet had physical strength comparable to ceramic membranes [11]. One inorganic material that met these needs was geopolymer [12].

Geopolymers were made from aluminosilicate with an amorphous polymer structure and an activator. Geopolymers had high chemical stability, good compressive strength, high durability, and high thermal stability [13], making them suitable for use in harsh environments. They were also environmentally friendly, being made from waste materials from various industrial and agricultural wastes [14], allowing a significant amount of waste material to be recycled into new products [15].

Geopolymer membranes had been widely applied in various fields such as seawater desalination [16], dye removal [17], tetracycline removal [18], ethanol-water separation [19], antibiotic removal [20], and others. The scanning mechanism of geopolymer membranes involved several processes, including size-based verification that prevented large molecules from passing through the membrane pores. Additionally, interactions with the membrane surface, such as hydrogen bonding or electrostatic interactions, could hinder contamination [21] This phenomenon made long-term use susceptible to fouling or clogging on the surface, thereby reducing membrane flux and performance [22].

Photocatalytic geopolymers combine the benefits of geopolymer technology with photocatalytic properties. Photocatalytic geopolymer materials utilize sunlight or artificial light to catalyze chemical reactions and promote the degradation of dye waste. The addition of photocatalytic properties to geopolymers could enhance hydrophilicity and add self-cleaning capabilities, as they could break down dye waste into smaller (or even non-toxic) substances without forming secondary pollutants and also decompose contaminants in the pores [23]. Conventional photocatalysts, such as TiO₂-based ones, often face challenges with low stability in extreme environments, which limits their efficiency and application range [24]. As an alternative, photocatalytic geopolymer offers the advantage of dual functionality, serving both as a mechanical filtration medium and as a chemical degradation agent for dye wastewater. Geopolymers have high chemical and physical stability under extreme pH conditions and high temperatures, making them more superior than traditional photocatalysts [13]. Furthermore, their low production costs and the use of waste-based raw materials enhance their economic feasibility and sustainability. By integrating membrane filtration capabilities with photocatalytic properties, photocatalytic geopolymers are expected to address one of the main challenges in membrane technology: fouling, which can reduce long-term performance.

Therefore, this article aimed to analyze photocatalytic geopolymer materials for the degradation of cationic and anionic dye waste, covering several approaches, including the synthesis of photocatalytic geopolymers, the application of photocatalytic geopolymers for the degradation of anionic and cationic dyes, factors influencing photocatalytic geopolymers for the degradation of anionic and cationic dyes, and a comprehensive review of significant challenges and potential future advancements in the field of photocatalytic geopolymers [25].

# SYNTHESIS OF GEOPOLYMER MEMBRANES

Geopolymers were amorphous materials that were easy to synthesize, had high availability of raw materials, were inexpensive, and could be applied in separation processes with high efficiency [26]. Geopolymers had advantages such as high chemical stability, good compressive strength, high durability, and high thermal stability [13]. The sustainable development goals drove the advancement of geopolymer materials because they could be synthesized from various industrial and agricultural wastes, allowing a significant amount of waste materials to be recycled into new products [15].

The synthesis process of geopolymer membranes involved directly mixing the precursor, alkaline activator solution, and pore-forming materials in deionized water. The resulting slurry was molded and dried, then cured at specific temperatures and times [27]. The precursors used in this process could be kaolin or solid industrial aluminosilicate wastes such as fly ash, granulated blast furnace slag, and steel slag. Table 1 presented the composition of several geopolymer precursors.

Table 1. Chemical Composition of Geopolymer Precursors

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Chemical composition | Kaolin | Metakaolin | Fly Ash | Furnace Slag | Bottom ash | Silica fume | Terak Baja |
| SiO2 | 54,98 | 52.80 | 22 | 34.39 | 61.2 | 87.60 | 21.90 |
| Al2O3 | 17.54 | 44.92 | 63 | 14.47 | 26.8 | 0.38 | 9.78 |
| Fe2O3 | 5.33 | 0.48 | 7.22 | 0.63 | 4.40 | 0.66 | 14.90 |
| CaO | 5.40 | 0.08 | 3.80 | 41.67 | 2.10 | 0.57 | 37.40 |
| MgO | 0.20 | - | 0.7 | 6.49 | 0.61 | 3.67 | 10.30 |
| SO3 | 0.00 | - | - |  | - | - | 0.60 |
| Na2O | 0.95 | - | 0.2 | 0.22 | 0.34 | 1.26 | 0.20 |
| K2O | 0.09 | - | 1.3 | 0.36 | 1.54 | 2.36 | 0.29 |
| TiO2 | - | 0.36 | 1.3 | 0.53 | 0.94 | - | - |
| P2O3 | - | - | - |  | 0.07 | - | - |
| ZnO | - | - | - | <0.01 | - | - | - |
| L.O.1 | 14.50 | 1.36 | - | - | 1.70 | - | - |
| Citation | [28] | [29] | [30] | [31] | [32] | [33] | [34] |

The activating base solution functions to break down the outer layer of the aluminosilicate source, allowing the dissolution of SiO₂ and Al₂O₃ species into the main components of geopolymer membranes, which are the silicate ions [SiO₄]⁴⁻ and aluminate ions [AlO₄]⁵⁻ tetrahedral [35]. The increase in alkalinity can accelerate the dissolution of particles from raw materials and form a gel. This gel can fill large pores and create a denser structure [36]. This aligns with the research conducted by Farhan (2019), which showed that activators with higher pH values can efficiently enhance the hydration process of geopolymer paste because Si-O and Al-O bonds are weaker in alkaline environments.

[37] On the other hand, excessively high concentrations cause an excess of monomers, making the reaction inefficient[38].

The geopolimerization mechanism was described by Davidovits (1994), where [AlO4] and [SiO4] groups underwent polycondensation, forming a polymer gel with three basic structural units. The gel transformed into a three- dimensional network structure (simultaneously forming a porous structure) after dehydration [39]. Polymer bonds were formed by monomer units depending on the silica/alumina ratio. Therefore, Table 1 revealed that the metakaolin precursor was an excellent material for geopolymer synthesis due to its highest SiO2 and Al2O3 compositions compared to other materials. Additionally, metakaolin had a consistent composition produced through strict control processes, making geopolymerization with metakaolin easier to control and allowing for adjustment of final material properties. In their performance as filtration membranes, geopolymer membranes were influenced by several factors: porosity and mechanical properties. Porosity was necessary to enhance permeability, water flux, and molecular diffusion, while the mechanical properties of the membrane could increase its lifespan. Thus, the synthesis of geopolymer membranes needed to be optimized to achieve membranes with uniform pores, even pore distribution,

and high mechanical strength.

The mechanical properties of geopolymers were influenced by the condensation process of geopolymer gel, which involved several parameters such as the Si/Al ratio, the R/Al ratio, and the Si/R ratio (R indicating Na+ or K+) [27. The molar ratio of Si/Al significantly affected the microstructure and mechanical properties of geopolymers. Si/Al ratios of 1, 2, and 3 corresponded to poly-sialate (-Si-O-Al-O-), poly-sialate-siloxo (-Si-O-Al-O-Si-O-), and poly- sialate-disiloxo (-Si-O-Al-O-Si-O-Si-O-) structures, respectively. The microstructure of geopolymer affects the surface charge of the geopolymer. Higher aluminum content can increase the density of positive charges on the surface, which is beneficial for attracting cationic dyes through electrostatic interactions. This is particularly important at certain pH levels, where the surface charge can be optimized for maximum dye adsorption [40]. Additionally, the Si/Al ratio also influences the hardness of the geopolymer membrane.

A higher Si/Al ratio resulted in higher compressive strength because silicon could form a more stable network compared to aluminum. Additionally, the stability of geopolymers increased with higher silicate content. However, an excess of silica led to reduced durability due to the formation of polysialate with lower mechanical properties and hardening. Excessive silica also led to the formation of more porous structures, negatively impacting material resistance and potentially lowering the mechanical properties of geopolymers due to excessive raw material reactivity

[41]. From Table 3, it was noted that a geopolymer with Si/Al ratio of 1.4, Na/Al ratio of 1, and Na/Si ratio of 1 exhibited good compressive strength.

**Table 2** Composition of Geopolymer Synthesis with Metakaolin Precursor on Compressive Strength

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **No** | **Ref** | **Precursor** | **Si/Al** | **Na/Al** | **Na/Si** | **Compressive strength (Mpa)** |
| 1 | [42] | Metakaolin | 1.20 | 1.92 | 1.280 | 0.5 |
|  |  |  | 1.80 | 1.123 | 0.635 | 12 |
|  |  |  | 2.20 | 1.192 | 0.54 | 23 |
| 2 | [43] | Metakaolin + red mud | 1.2 | 0.8 |  | 9 |
|  |  |  |  | 0.9 | 48 |
|  |  |  |  | 1 | 56 |
|  |  |  |  | 1.1 | 52 |
|  |  |  |  | 1.2 | 45 |
|  |  |  |  | 1.3 | 40 |
| 3 | [44] | Metakaolin + Zeolit |  |  | 0.7 | 7 |
|  |  |  | 0.8 | 13 |
|  |  |  | 0.9 | 18 |
|  |  |  | 1 | 22 |
|  |  |  | 1.1 | 16 |
|  |  |  | 1.2 | 6 |
| 3 | [45] | Metakaolin + Fly ash | 1.2 | 0.4 |  | 60 |
|  |  |  | 1.3 |  | 58 |
|  |  |  | 1.4 |  | 70 |
|  |  |  | 1.5 |  | 44 |
| 4 | [46] | Metakaolin | 1 |  |  | 0.2 |
|  |  |  | 1.25 | 0.28 |
|  |  |  | 1.5 | 0.7 |

The addition of Na to geopolymers in the form of an alkaline activator solution played a significant role in reactivity, pore structure, and the formation of aluminosilicate gel, thereby influencing the mechanical and chemical properties produced. Hydroxide ions in NaOH activated SiO2 and Al2O3 from the particle surfaces, forming Si(OH)4- and Al(OH)5- monomers [47], [48], [49]. Therefore, the concentration of NaOH was also crucial to consider. A low concentration of NaOH resulted in fewer Si(OH)4- and Al(OH)5- monomers being formed, thus reducing the mechanical strength of geopolymers [50]. Additionally, higher concentrations of NaOH could enhance the hydration process of geopolymer paste because weaker bonding strengths of SiO and Al-O in basic environments cause more silicon and aluminum ions to dissolve [51]. This could inhibit the formation of monomers, where an excessive amount of OH-ions could increase viscosity, thereby making the reaction inefficient [38], [47], [52], [53].

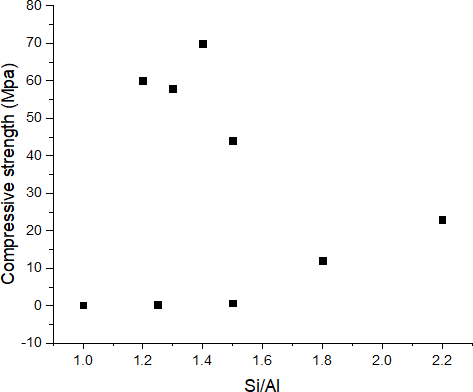
Another factor that affects membrane performance is pore structure and surface area. Pores in geopolymer membranes are created using the direct foaming method, which involves directly mixing pore-forming agents into geopolymer paste. Subsequently, these agents react with alkali and generate gas to form a porous microstructure in the geopolymer. H2O2 has been widely used as a foaming agent due to its low cost, wide availability, and easy reproducibility in synthesis.

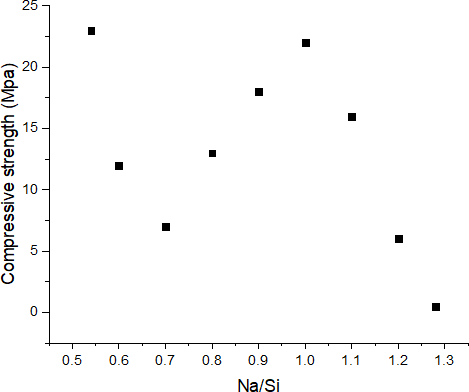
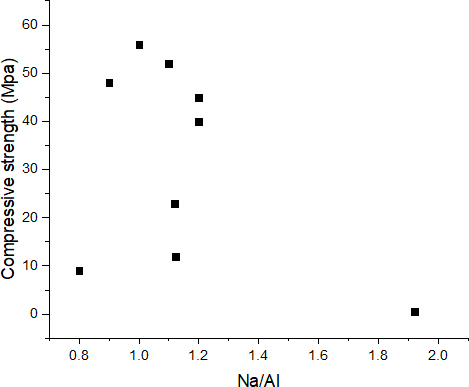
Table 3. shows that the optimal percentage of H2O2 is 3% because it exhibits good porosity and high compressive strength. H2O2 forms gases (O2 and H2) and other by-products through chemical reactions, which are then trapped in the geopolymer paste and result in pores, as illustrated in the following reaction:

H2O2 + OH- → HO2- + H2O (1) HO2- + H2O2 → H2O + O2 + OH- (2)

Porosity affects membrane performance because the functioning mechanism of geopolymer membranes depends

on pore size. Molecules larger than the membrane pores will be blocked due to size differences, as well as the electrostatic interactions between contaminants and the charges of the geopolymer [21]. An increase in the number of pores within the membrane can enhance its permeability, thus supporting optimal membrane performance. However, the presence of large-sized pores may have a negative effect, as it can potentially reduce the membrane's rejection properties [54]. A good membrane will produce high flux and rejection. Flux refers to the amount of species that can pass through the membrane, while rejection refers to the amount of species rejected by the membrane surface.





**Figure 1** The influence of Si/Al, Na/Al and Na/Si on the compressive strength of geopolymer

The porosity produced in geopolymers ranges in size from nanometers to millimeters but does not connect the pores to each other [55]. The majority of pores in geopolymers are distributed in sizes ranging from 2 nm to over 10 μm [56]. Pores larger than 10 μm are macropores resulting from the addition of foaming agents like H2O2. This finding is consistent with the research by Cilla, Morelli, and Colombo (2014), indicating that gases produced from hydrogen peroxide decomposition serve only to increase pore size in geopolymers and form closed pores. These intentionally introduced bubbles are stable and evenly distributed within the binder, enhancing resistance to freeze-thaw cycles and reducing thermal conductivity, making geopolymers suitable for applications in both cold and hot environments [56]. Macropores resulting from H2O2 decomposition are easily accessible by water during porosity measurements using Archimedes' principle [58].

Geopolymers also contain capillary pores, typically associated with internal pores. These are produced from air bubbles trapped in the paste during dissolution and polycondensation processes. Internal pores range in size from 0.1 μm (100 nm) to 10 μm and include meso and micro pores that are interconnected through a finer gel pore network, creating a "bottle ink" effect in geopolymers. Therefore, porosimetry analysis reveals that large pores are covered by finer gel pores in geopolymers. These meso and micropores can contribute to microcrack formation, thereby reducing mechanical strength and elastic modulus. Abundant nano-scale pores have been identified as a characteristic feature of geopolymers [59], representing interstitial spaces left between granular aluminosilicate gel groups (typically ranging in characteristic size from 2 nm to 100 nm), forming a network of nano-scale pores.

**Table 3.** The influence of H2O2 addition on the porosity and compressive strength of geopolymers.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **No** | **Material** | **pore forming** | **Porosity** | **Compressive strength (Mpa)** | **Ref** |
| 1 | Metakaolin/ Fly Ash | H2O2 3%  5%  7% | 68%  80%  85% | 3.3  2.4  1.3 | [60] |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **No** | **Material** | **pore forming** | **Porosity** | **Compressive strength (Mpa)** | **Ref** |
| 2 | Metakaolin | H2O2  2.65 g  1.80 g  1.10 g | 64.7%  55.6 %  52.7 % | 0,8  2  5.5 | [61] |
| 3 | Kaolin | H2O2  1 %  2 %  3 %  4 %  5% | 61,90  75,60  79,50  83,20  85,30 | 7,70  1,80  0,90  0,80  0,30 | [62] |
| 4 | Metakaolin | H2O2 1%  2 %  3%  4%  5 % | 70,70  77,00  81,90  85,70  88,80 | 6,90  3,20  1,70  1,30  0,80 | [63] |
| 5 | Metakaolin | H2O2 1.5%  3.0%  6.0% | 39.77  45.7  60.7 | 0.25  0.3  0.18 | [64] |

# SYNTHESIS OF PHOTOCATALYST GEOPOLYMERS

Membrane was designed to have the ability to break down or decompose organic and inorganic pollutants when exposed to light, particularly ultraviolet (UV) light. The addition of photocatalysts to the geopolymer membrane could have been an effective strategy to prevent fouling [65]. Fo uling was the accumulation of unwanted materials on the surface of the membrane, which reduced its efficiency and performance. Photocatalysts, such as titanium dioxide (TiO2) or zinc oxide (ZnO), could decompose organic materials and microorganisms that cause fouling when exposed to UV or visible light. The key value of the photocatalytic geopolymer material heavily depended on the photocatalyst agents that functioned to break down organic or inorganic compounds under light radiation. The geopolymer precursors also contained several photocatalytic agent compounds such as SiO2, Al2O3, Fe2O3, and TiO2, as seen in Table 1. The photocatalytic activity could be enhanced by adding some metal oxides or carbon derivatives into the matrix during the elaboration process, such as CdS [66], ZnO[67],, Cr2O3 [67],, Fe2O3[68],, graphene oxide[69], and TiO2 [25]. The synthesis of photocatalytic geopolymers used different methods, as shown in Table 4.

**Table 4** Methods for Adding Photocatalyst to Geopolymer Membranes

|  |  |  |  |
| --- | --- | --- | --- |
| Synthesis Method | Aspects that require consideration | | Ref |
| Preparation principle | Preparation technique |
| Film coating | Film coating was performed using the dip-coating method, where the geopolymer membrane was immersed in the photocatalyst solution and  pulled at a specific speed. | The withdrawal speed and viscosity of the photocatalyst solution could influence the thickness of the formed layer. | [70] |
| In situ | The photocatalyst was added simultaneously with the geopolymer precursor, then the activator solution was added and mechanically stirred. | The procedure was straightforward and uncomplicated, as all components used in the synthesis were mixed. | [71] |
| Impregnation | The photocatalyst passed through the membrane pores, thus being trapped within the pores and on the membrane surface, forming sedimentation which  was then calcined. | Careful consideration of the photocatalyst solution concentration and soaking time is needed to prevent pore agglomeration | [72] |

The in-situ method had a simpler synthesis procedure compared to other methods because the photocatalyst agent was added directly into the geopolymer precursor mixture, which meant the fabrication costs were expected to be lower. Additionally, it had high reproducibility and more uniform photocatalyst distribution, but it required optimization of photocatalyst loading to prevent agglomeration that could block the geopolymer pores. Furthermore, the photocatalytic activity depended on the distribution of the photocatalyst within the geopolymer.

The film coating method required high fabrication costs and scalability, and careful consideration of the withdrawal speed and viscosity of the photocatalyst sol, which affected the thickness of the layer on the surface. Consequently, its reproducibility was considered lower than that of the in-situ method, with the photocatalyst being dispersed only on the surface. The photocatalytic activity depended on the thickness of the layer on the surface.

The impregnation method required high fabrication costs and scalability, with careful consideration of the photocatalyst solution concentration and immersion time to avoid agglomeration in the pores. As a result, its reproducibility was considered lower than that of the in-situ method, with non-uniform photocatalyst dispersion that could affect the photocatalytic activity.

# PHOTOCATALYST GEOPOLYMER MEMBRANES FOR DYES DEGRADATION

The degradation mechanism of cationic and anionic dyes by photocatalytic geopolymers involved a series of interconnected stages. It started with filtration and adsorption, followed by the photogeneration of charge carriers and charge separation. This process then involved the formation of reactive species that decomposed the dyes. Finally, the degradation products are desorbed from the surface, allowing the degradation cycle to continue. Initially, the photocatalytic geopolymer material underwent a filtration process that included size exclusion, where particles or molecules larger than the membrane pores were retained on the surface or within the membrane pore structure. Then, hydrophobic interactions occurred, where the hydrophobic groups of dye molecules tended to interact and adhere to the membrane surface, which also had hydrophobic properties. Adsorption followed, where dye molecules bonded to the membrane surface through various interactions, including electrostatic bonding, hydrogen bonding, and van der Waals interactions [73].

During the photogeneration of charge carriers and charge separation, irradiation of the photocatalyst caused electron excitation from the valence band (VB) to the conduction band (CB) due to artificial or sunlight irradiation, creat ing positive holes (h+) in the VB [66], according to the following equation:

FK + hυ → e− + h+ (1)

The electron then reacted with the adsorbed O2 molecules on the photocatalyst surface, forming superoxide ions (O -

2

) according to equation 2.

O2ads + e− →O2⋅−ads (2)

Subsequently, the dye waste was oxidized by O - ions and degraded into inorganic or non-toxic substances [74] as described in the following equation:

2

2O ⋅− + 2H O→2OH⋅ + 2OH− + O (3)

2 ads 2 2

OH− ads + h+→OH⋅ads (4)

h+ + Pollutant→Pollutant+ (5)

Additionally, electrons also reacted with H2O and pollutants adsorbed on the photocatalyst surface, degrading the catalyst according to equations 6 and 5.

H2Oads + h+→ H+ + OH◦ads (6)

The highly reactive hydroxyl radical OH⋅ads and superoxide radical O2⋅−ads attacked and broke chemical bonds within dye molecules. This process decomposed the dyes into simpler products, including water, carbon dioxide, and other inorganic ions. After degradation, the simpler degradation products are desorbed from the geopolymer surface. This desorption reopened active sites on the geopolymer surface, making it ready for the next degradation cycle.

Dye waste can be classified into cationic and anionic dyes. Cationic dyes are basic dyes, while anionic dyes include direct, acid, and reactive dyes [75]. Anionic and cationic dyes have different chemical structures and properties that can influence their degradation processes by photocatalytic geopolymers

**Table . 5** Photocatalytic geopolymers for degradation of cationic and anionic dyes

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Precursor** | **photocataly st** | **Dye type** | **Dye waste** | **Initial concentration**  **of dye waste (M)** | **pH** | **Time (minutes)** | **%**  **Degradation Efficiency** | **Ref** |
| Fly ash | *graphene oxide* | cationic | Methylene Blue | 0.01 |  | 120 | 99 | [69] |
| Fly ash |  | cationic | Methylene Blue | 4.01 × 10 −6 |  | 250 | 92.79 | [76] |
| Bottom ash | Mn2+ yang mengandung Cu | cationic | Sky Blue 5B | 1 |  | 100 | 100 | [77] |
| Al2O3–SiO2 | CdS-Fe2O3 | cationic | Methylene Blue | 0.02 | 12 | 25 | 99 | [78] |
| Furnace Slag | Graphene | cationic | Metil Viole | 0.004 |  | 110 | 91.6 | [79] |
| kaolin | Zeolit-TiO2 | cationic | Methylene Blue | 0.004 |  | 120 | 99.1 | [80] |
| Metakaolin- silika foam | Cr2O3 | cationic | Basic Green | 0.03 | 7–7,5 | 100 | 100 | [72] |
| metakaolin | PEG-TiO2 | cationic | Methylene Blue | 0.05 |  | 25 | 98 | [81] |
| Metakaolin | ZnTiO 3 /  TiO 2 | cationic | Methylene Blue | 0.02 | 7 | 90 | 98.5 | [83] |
| Tanah Liat | TiO 2 | cationic | Rhodamin B | 0.005 | 9 | 90 | 97 | [84] |
| Metakaolin | TiO 2 | cationic | Methylene Blue | 0.0001 | 9 | 120 | 95 | [85] |
| Tanur Sembur | CdS | cationic | Methylene Blue | 0.02 | 12 | 100 | 88 | [86] |
| Metakaolin | Kitosan | cationic | Krital violet | 0.03 | 7 | 120 | 93 | [17] |
| Al2O3–SiO2 | CdS | anionic | Methylene Orange | 0.005 | 7 | 90 | 92.5 | [66] |
| Slag LD | ZnO | anionic | Congo Red | 1 | 6 | 60 | 93 | [67] |
| Fly ash | graphene elektrokondu ktif | anionic | Indigo Carmine | 0.01 |  | 90 | 90 | [71] |
| Furnace Slag | Fe2O3 | anionic | Congo Red | 0.02 |  | 100 | 100 | [87] |
| Magnesium Slag | NiO dan CuO | anionic | Indigo Carmine | 0.001 |  | 60 | 100 | [88] |
| Fly ash | TiO2 | anionic | Congo Red | 0.02 | 5 | 120 | 98 | [89] |
| Kaolin | Fe2O3 | anionic | Congo red | 0.02 | 2 | 60 | 100 | [90] |

From Table 5. it can be observed that Geopolymer photocatalysts are capable of removing both types of dyes with an average degradation efficiency of 96.23% for cationic dyes and 96% for anionic dyes. This efficiency is linked to the presence of negatively charged aluminum in the geopolymer microstructure, which affects dye interaction with the photocatalytic geopolymer membrane. Moreover, the efficiency also depends on factors such as the solution's pH, the initial concentration of dye waste, contact time, photocatalyst dosage, and the type of photocatalyst used

## Effect of pH

The pH level of the solution could control the magnitude of the electrostatic charge carried by ionized dye molecules. Additionally, pH was a crucial factor in the photocatalytic process because it affected the surface

charge of the photocatalyst, the degree of ionization of target organic pollutants, and the dissociation of functional groups at the photocatalyst's active sites. Table 3 indicated that photocatalytic geopolymers had significant potential for degrading both cationic and anionic dyes, with high degradation percentages observed in various research studies.

Degradation of cationic dyes was performed at high pH (>7) levels because, at such levels, the positive charge at the interface decreased and the surface of the photocatalytic geopolymer became negatively charged [75]. pH played a crucial role in the photocatalytic process, influencing the surface charge of the photocatalyst, the ionization degree of target organic pollutants, and the dissociation of functional groups at the photocatalyst's active sites. This finding was consistent with Asim et al. (2022), who studied the effect of pH variation (3, 5, 7, 9) on the efficiency of methylene blue dye removal, noting that pH 7 and 9 exhibited higher removal efficiencies, up to 95%. Additionally, another study [75] on Rhodamine B dye degradation at pH 3, 6, and 9 found that pH 9 achieved a higher removal efficiency of 90% due to stronger electrostatic interactions in a basic environment (pH = 9) between the catalyst and the dye. Moreover, a high-pH solution promoted the production of hydroxyl radicals on the semiconductor surface, stimulating photocatalytic activity.

Conversely, the degradation process of anionic dyes was carried out at low pH (<7) levels because, at such levels, the surface of the geopolymer photocatalyst became more positively charged, facilitating strong electrostatic bonds. This observation was supported by Asim et al. (2022). Sarkar, Basu, and Samanta (2021) conducted research on Congo red dye degradation using ZnO/LDSGP photocatalytic geopolymer at various pH levels (4, 6, 8, 10), identifying pH 6 as optimal due to the outer surface of the ZnO/LDSGP nanocomposite becoming negatively charged at pH levels above 6, thereby repelling anionic Congo red dye. Furthermore, Gajera et al. (2022) investigated the application of MFA photocatalytic geopolymer for Congo red (CR) dye degradation at pH 2, 4, 6, 8, 10, and 12, determining pH 5 as optimal for Congo red degradation due to significant negative charge production from dye ionization. Many hydroxyl ions adsorbed onto the geopolymer surface, weakening the electrostatic attraction between the dye and the photocatalytic geopolymer. Therefore, acidic solutions supported strong CR adsorption onto the modified geopolymer surface.

## The influence of the initial concentration of dye wastewater

The initial concentration of dye wastewater influences the percentage of dye removal. This is directly related to the interaction between the dye and the geopolymer surface, as higher dye concentrations can lead to fouling or blockages. Such blockages can reduce the diffusion rate of dye molecules within the geopolymer, thus decreasing flux values. Therefore, adding photocatalysts to the geopolymer promotes self-cleaning and reduces surface fouling, enhancing its hydrophilicity.[91]. Additionally, dye concentration also influences the photocatalysis process [87].

For cationic dyes, the percentage of dye removal decreases with increasing dye concentrations. This aligns with Ji et al. (2021) study on the influence of varying initial concentrations of methylene blue on dye degradation percentages. It was found that methylene blue underwent complete degradation within 30 minutes at low concentrations (<20 mg/L), with degradation time increasing as initial MB concentrations rose. Moreover, solution transmittance decreases with increasing dye concentration, obstructing light due to dye concentration, which can interfere with the photocatalysis process. Ji et al. (2021) further explained the impact of varying initial concentrations of dye wastewater (10 mg/L, 20 mg/L, 30 mg/L, and 40 mg/L), showing the highest dye degradation percentage at 10 mg/L, attributed to weakened solid-liquid interface driving forces at low concentrations. Color concentration and transparency affect the performance of the photocatalytic degradation system.

Anionic dyes experience similar conditions. This corresponds with Y. J. Zhang et al.(2013) study on Congo red dye degradation using geopolymer modified with Fe2O3 at varying initial concentrations of Congo red (CR) (2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L, and 10 mg/L). CR dye at an initial concentration of 2 mg/L showed the highest degradation activity compared to other CR solutions in the initial reaction stage. Diluted CR solutions with bright colors can enhance light utilization efficiency in the photocatalysis process. Additionally, Sarkar, Basu, and Samanta (2021) explained the degradation of CR dye by geopolymer modified with ZnO at varying initial CR concentrations (5 mg/L, 10 mg/L, 15 mg/L, and 20 mg/L), achieving maximum photodegradation efficiency at an initial CR concentration of 5 mg/L. Lower CR concentrations result in lighter colors that can enhance CR dye photodegradation processes.

## The influence of contact time

Contact time influenced the percentage of dye removal as it determined the equilibrium time. Equilibrium time is the time required for maximum degradation, where degradation remains constant [92]. The percentage of color degradation increased with contact time and stabilized at a certain level. In the study by Gajera et al. (2022), differences in stable degradation times were studied for Congo red (CR) and methylene blue (MB) dyes using geopolymers made from fly ash/TiO2 modified with chitosan. It was found that the degradation time for CR dye gradually stabilized after 120 minutes, while for MB dye, the degradation time stabilized after 180 minutes. Sarkar, Basu, and Samanta (2021) studied the degradation of CR dye using geopolymers modified with ZnO and found a stable degradation time of 30 minutes.

## Photocatalyst dosage

The dosage of photocatalysts added to geopolymers also influenced the percentage of dye wastewater degradation because dye degradation correlated positively with the electroconductivity of the photocatalyst and its light absorption capacity. Higher concentrations could enhance degradation efficiency, but there was an optimal concentration limit to prevent particle agglomeration and reduce photocatalytic efficiency.

According to Ji et al. (2021), who studied the effect of varying CdS weight percentages (2%, 4%, 6%, and 8%) in geopolymers for methylene blue (MB) dye degradation, CdS at 4% weight showed superior photocatalytic activity compared to other samples, which was directly related to its light absorption capacity. UV-Vis DRS test results indicated that the red shift increased with increasing CdS content from 0% weight to 4.0% weight. Further addition of CdS nanoparticles (>4.0% weight) reduced the absorption capacity of geopolymers due to CdS nanoparticle agglomeration within the geopolymer matrix.

For anionic dyes, as shown in Y. J. Zhang et al (2018) study on the influence of graphene (GR) percentage variations in geopolymers for indigo carmine dye degradation, it was found that 1.0% GR had a higher dye degradation percentage compared to 0.7%, 0.4%, and 0.1% GR due to its lower water dispersion. Additionally, graphene and geopolymers formed a coupling system where photogenerated electrons from Fe2O3 semiconductors in geopolymers were efficiently transferred to graphene, thus separating photogenerated electron-hole pairs efficiently and enhancing photocatalytic degradation efficiency. Therefore, higher percentages of GR increased dye degradation percentages.

## Photocatalytic Types

The ability of geopolymers to degrade dyes is influenced by the type of photocatalytic agent due to differences in band gaps. The band gap energy of photocatalytic agents determines the wavelength of light that can be absorbed and utilized for photocatalytic reactions. Therefore, selecting a photocatalytic agent with an appropriate band gap energy is crucial for efficient dye degradation by geopolymers, as shown in Table 6, which outlines the band gaps of various types of geopolymers. According to Table 6, Mn has a small band gap, making it effectively usable in visible light. A wide band gap restricts the use of visible light because the photon energy in the visible spectrum may not be sufficient to promote electrons from the valence band to the conduction band [93].

**Table 6.** Band gap of photocatalytic geopolymers

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Precursor** | **photocatalyst** | **Band Gap (eV)** | **Degradation Efficiency** | **Ref** |
| Al2O3–SiO2 | CdS | 3,85 | 99 % | [66] |
| Furnace Slag | CdS | 3.20 | 99,9 % | [86] |
| Fly ash | graphene oxide | 3.38 | 99 % | [69] |
| Slag LD | ZnO | 2.95 | 93 % | [67] |
| Fly ash | graphene elektrokonduktif | 3.47 | 90 % | [71] |
| Furnace Slag | Fe2O3 | 1.9 | 100 % | [87] |
| Magnesium Slag | NiO dan CuO | 3.16 | 100 % | [88] |
| Fly ash | TiO2 | 3.2 | 98% | [89] |
| Al2O3–SiO2 | CdS-Fe2O3 | 3,85 | 99% | [78] |
| Metakaolin | graphene oksida | 3.20 | 93 % | [94] |

In research Zehua, et al (2022), it was found that CdS could be used for the degradation of various dyes, including Crystal Violet (CV), Rhodamine B (RhB), and Methyl Orange (MO). The removal performance followed the order of CV > MB > RhB > MO. The adsorption effect of the geopolymer membrane on organic dyes varied due to the surface charge of each dye. Anionic dye MO could not be effectively adsorbed by the geopolymer membrane because the aluminum in the geopolymer membrane had a negative charge. This resulted in better interactions with cationic dyes.

# PERSPECTIVES AND FUTURE CHALLENGES FOR GEOPOLYMER PHOTOCATATALYST

The photocatalytic degradation process of cationic and anionic dyes by geopolymers involved a series of complex reactions influenced by reaction conditions, geopolymer characteristics, and dye properties. The environmental pH level played a crucial role in the degradation of both anionic and cationic dyes. Anionic dyes were more stable at an acidic pH, while cationic dyes were more stable at an alkaline pH. The degradation time of dyes by geopolymers was relatively long. Developing more efficient photocatalytic agents and geopolymer matrices was essential to reducing reaction times. Optimizing the dosage of photocatalytic agents in geopolymer matrices was crucial for achieving high efficiency and stability in degradation. Developing geopolymers with better selectivity for specific anionic and cationic dyes was crucial for preventing the degradation of non-target compounds. Furthermore, the environmental impact of pollutants during the photocatalytic degradation process and the potential formation of by-products should be thoroughly examined and discussed. Moreover, the impacts of heavy metal leaching, such as Cd, Zn, or Ti used in photocatalytic systems, needed to be examined, including mitigation strategies or post-treatment measures. Economic feasibility studies and life cycle assessments should be conducted to evaluate the cost-effectiveness and environmental sustainability of using geopolymers for dye wastewater degradation.

# CONCLUSION

In recent years, many articles have been published on the utilization of geopolymers as photocatalysts for dye wastewater degradation, leading to numerous assumptions and findings. Photocatalytic geopolymer offers the advantage of dual functionality, serving both as a mechanical filtration medium and as a chemical degradation agent for dye wastewater. This review aims to analyze the influence of dye types and discuss several studies on dye degradation by geopolymers. It provides a simple comparison between the degradation of cationic and anionic dyes using geopolymers as photocatalysts. It can be concluded that Geopolymer photocatalysts are capable of removing both types of dyes with an average degradation efficiency of 96.23% for cationic dyes and 96% for anionic dyes. This efficiency is linked to the presence of negatively charged aluminum in the geopolymer microstructure, which affects dye interaction with the photocatalytic geopolymer membrane. Moreover, the efficiency also depends on factors such as the solution's pH, the initial concentration of dye waste, contact time, photocatalyst dosage, and the type of photocatalyst used. The most crucial factor affecting dye wastewater degradation is pH, where higher pH values are preferable for adsorbing cationic dyes, while lower pH values are preferable for adsorbing anionic dyes. It is also known that the dosage of photocatalytic agents influences the effective concentration of dyes for removing both cationic and anionic dyes, but exceeding the optimum point can cause agglomeration. The type of photocatalytic agent also affects the percentage degradation due to differences in band gaps. Comparing the cost of degrading cationic and anionic dyes by geopolymers is crucial for evaluating the dye degradation process from an economic perspective.

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