Application of low-cost mesoporous geopolymer for dye waste removal

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Abstract. Environmental pollution causes a significant reduction in water quality. Sustainable development and industrial waste pollution are the supporting factors for the amount of water that is not suitable for consumption. Contaminants in wastewater that pollute water sources include phenolic compounds, substituted compounds, various types of pesticides, and dyes. This study focuses on developing geopolymers as a low-cost alternative adsorbent for adsorbing harmful dyes. Geopolymers can rapidly absorb dyes due to their supportive surface properties to absorb dyes. The porous structure is derived from alumino-silicate materials such as kaolin, metakaolin, dolomite, fly ash, and slag which have been activated with alkaline or alkaline silicate solution. Geopolymers are readily stored adsorbents. Geopolymers have shown good adsorption capacity of the dyes of Methylene blue, Rhodamine B, Congo Red, Methyl Orange, Methyl Violet. This study aims to provide an overview of the types of geopolymer forming materials, geopolymer characterization, application of geopolymers as dye adsorbents, and comparison with other adsorbents. The adsorption isotherm model and adsorption kinetics are also summarized in this overview.

Keywords: Geopolymer; Adsorbent; Dye waste

1. Introduction

Water is one of the basic needs which is a very important facility in human life to support life. The most vital resource for its existence is in social, economic, and environmental life. The existence of water that has been contaminated by factory waste causes water to not be consumed because it contains substances chemicals and dyes that can cause various diseases. Industrial wastewater that contains dyes is a common problem in the environment [1]. The discharge of dye in industrial waste becomes a crucial problem because it pollutes water [2]. Dye contamination in liquid industrial wastes is due to containing complex pollutants and high color intensity making it difficult to degrade, even in the long term with biodegradation [3].

In the textile industry, about 15% of the dye operation does not even stick to the fabric fibers and
becomes waste [4]. With the problem of wastewater pollution, there needs to be a way to remove dye waste [5]. Various technologies have been developed to remove dye waste such as adsorption [6] - [17], electrochemistry [18], coagulation [19], exchange ion [20] [21], photocatalytic degradation [22] - [28], biodegradation [29], oxidation [30] and photocatalytic sterilization [31]. The methods for treating the dye waste that is most widely used are the adsorption process, the adsorption process is widely used because of its low price, easy application, does not require energy, is non-toxic, simple design and a large amount of time estimation are very appropriate choices to select the process as a dye remover [32] [23]. Adsorbent material by utilizing industrial waste such as geopolymer is the right choice and has been developed by several researchers [33]. Joseph Davidovits as the inventor and developer of geopolymerization, coined the term "geopolymer" to classify the newly discovered geosynthetic and produce inorganic polymeric materials there are now used for some industrial applications [34]. These inorganic polymers are fast becoming the prima donna in industries because renewable materials are light, porous, do not produce new waste [35] so that geopolymers can be widely used in various fields such as protective coatings, plane, building materials, and starting to be researched for materials in the field of waste treatment as immobilization of hazardous materials [36] it is proven that geopolymers can produce higher adsorption capacities [3], [10]. Moreover, materials that can synthesize geopolymers can be obtained easily such as fly ash [3], [37] - [42], metakaolin [43] [44], kaolin [36], slag [45] [46], dolomite [47], red mud [46] [47] and biomass ash (rice husk ash [31], palm oil fuel ash [50] - [54], bamboo ash [55].

The use of geopolymers for dye removal in liquid waste is developing very well because many researchers provide updates to improve the performance of these materials. The main purpose of this article is to provide information on the latest developments in the extent to which geopolymers are an alternative economical adsorbent that can replace zeolite in the application waste treatment to adsorb dyes. This article critically reviews the effectiveness of geopolymers that can be used as adsorbents under the parameters of the geopolymer-forming material, type of dyes, adsorption capacity, adsorbent characterization, and comparison with other adsorbents are also discussed in this article. Despite several articles and reviews such as a review of the economical activated carbon-based adsorbent for the removal of dyestuff waste [56]; geopolymer material adsorbent to remove rhodamine b from textile waste [57]; removal of organic potassium by fly ash based adsorbent [37]; and leaf-based adsorbents for adsorbing dye [32], but those presented are still incompatible with current information. This review provides more relative information and focuses more on the adsorption of various colors from wastewater by geopolymers. New aspects of this review article include the types of geopolymer-forming materials commonly used to adsorb dyes, current research conditions, application and presentation of dye adsorption with critical analysis and identifying the comparison of geopolymers with other adsorbents. The author tries to provide information on a very good relationship between natural use and synthetic adsorbents in removing water pollutants, by using geopolymers to remove dyes in wastewater.

2. Raw Materials for Geopolymer
Geopolymer adsorbent is a relatively new type of adsorbent which has a porous structure and has the same characteristics as zeolite. These inorganic polymers result from the reaction of active aluminosilicates with alkaline solutions (Figure 1).
Figure 1. Schematic of geopolymer formation [58].

Geopolymerization occurs due to geosynthetic reactions that chemically integrate minerals. The mixing ratio of the aluminosilicate materials and activator solutions plays an important role in the formation of geopolymers, generally the weight ratio used is between 2.5 and 3.5 [58]. Geopolymers are characterized by a two to three-dimensional Si-O-Al structure, the framework of the geopolymer consists of polymeric Si-O-Al, similar to zeolite. Geopolymerization occurs at temperatures of about 60 °C or slightly higher, where leaching of the solid aluminosilicate feedstock in an alkaline solution leads to transfer of leached species from the solid surface into the gel phase [59], followed by nucleation and condensation of the gel phase to form fastener [60]. The microstructure of the geopolymer at the nanometer scale observed by TEM consisted of small aluminosilicate clusters with pores scattered in a highly porous tissue. Exposure to aluminosilicate materials such as fly ash, blast furnace slag, or a substance that is thermally activated to a high alkaline environment gives rise to the formation of geopolymers is called geopolymerization reactions. The basic geopolymerization process is described in the reaction 1 to reaction 3 below [61].

\[
\begin{align*}
(Si_2O_3, Al_2O_3)_n + 3nH_2O & \xrightarrow{NaOH/KOH} n(OH)_3 - Si - O - Al^{++} - (OH)_3 \\
& (Orthosialate) \\
\end{align*}
\]

\[
\begin{align*}
(n(OH)_3 - Si - O - Al^{+} - (OH)_3) & \xrightarrow{NaOH/KOH} (Na, K) - \left(-\frac{Si}{O} - O - \frac{Al}{O}^{++} - O\right)n + 3nH_2O \\
& (Na,K) Poly(sialate) \\
\end{align*}
\]

\[
\begin{align*}
(Si_2Al_2O_5)_n + 2nSiO_2 + 4nH_2O & \xrightarrow{NaOH/KOH} n(OH)_3 - Si - O - Al^{+} - O - Si - (OH)_3 \\
& (Ortho(sialate-siloxy))
\end{align*}
\]

The schematic above illustrates the presence of alkali metal ions (Na\(^+\), K\(^-\)) needed to offset the negative charge from the presence of Al. The nature of geopolymers is influenced by the characteristics of raw materials such as industrial waste, natural minerals, and their mixtures which are materials for conventional geopolymers. The raw material for geopolymerization can be natural minerals classified as aluminosilicates containing Si, Al, O, and other possible elements [62]. The chemical composition of the earth's crust is rich in silica and alumina and is an important source of
available raw materials for geopolymerization reactions. The adsorption process using geopolymers provides an attractive alternative to wastewater treatment, mainly because the adsorbents are cheap and do not require additional pretreatment before application. The following is a geopolymer forming material that can be used to adsorb dyes.

2. 1 Fly ash
Fly ash, as an industrial byproduct of burning pulverized coal, consists of unburned carbon particles and aluminosilicate particles collected by an electrostatic separator before being discharged into the atmosphere. Fly ash is known as one of the waste materials that cause environmental pollution in the form of water. In the past, the method commonly used to manage fly ash is to be disposed of in landfills. Environmental hazards occur due to the disposal of fly ash. Whereas solid waste, which is mostly residue from power plants, has great potential as an alternative to environmental applications such as zeolites as adsorbent of liquid waste in wastewater treatment [37] [7]. Fly ash as an economical adsorbent has been widely tested for its feasibility to adsorb pollutants [38], [41], [42]. Geopolymer synthesis based on fly ash with alkaline activating reactions is recognized as one of the best ways to utilize fly ash because of its low-cost benefits, environmentally friendly, energy-efficient, and recycle resources [39]. The highest photocatalytic activity for Nitric Oxide degradation in fly ash-based geopolymers dried at room temperature [63]. The differential pore size distribution of the geopolymer based on fly ash centered at 387 nm is useful for the adsorption and diffusion of methylene blue (MB) molecules. Methylene blue geopolymer based adsorbent fly ash showed a maximum removal at 37.04 mg/g, with variations in the effect of pH, initial dye concentration, adsorbent dose, contact time and temperature. The adsorption of methylene blue followed second-order kinetics and Langmuir model [64]. Geopolymer synthesized by alkaline activated fly ash was first used as a new photocatalyst for the degradation of methylene blue dye from wastewater. Geopolymers consist of nanoparticles with an average particle size of about 50 nm. More than 90% of the pore volume of fly ash-based geopolymers is mostly concentrated in the pore size in the 17–700 nm range [33]. Alkaline synthesized geopolymers based on fly ash from calcined coal bales using NaOH:Na$_2$SiO$_3$ solution with a ratio of 1:9 can efficiently absorb rhodamine B (RB) with variations in geopolymer dose and contact time [57]. The application of fly ash-based geopolymer for MB adsorption has an equilibrium of up to 120 minutes by batch experiment [65].

2. 2 Kaolin
The active geopolymer of kaolin (Al$_2$O$_3$,2SiO$_2$,2H$_2$O) can remove methyl orange from aqueous solutions with a surface area of 20.181 m$^2$/g [66]. The sol-gel method with synthetic kaolinite from tetraethylorthosilicate (Si(OC$_2$H$_5$)$_4$) and aluminum isopropoxide (Al(OCH(CH$_3$)$_2$)$_3$) shows that the content of kaolinite varies with synthesis conditions and has spectroscopic characteristics similar to that of natural kaolinite [67]. The batch adsorption technique used to remove methylene blue with the influence of process variables including contact time, pore diameter, dose, initial dye concentration, pH, stirring speed and solution temperature resulted in an adsorption equilibrium achieved in 360 minutes, and adsorption capacity of 30.8 mg/g by following first-order kinetics, Freundlich isotherms and Langmuir isotherms [68].

2.3 Metakaolin
Metakaolin is an anhydrous aluminosilicate clay mineral with a chemical composition of Si$_2$O$_5$, Al$_2$O$_3$ which is formed by a tetrahedral silica layer and an octahedral alumina layer. Some researchers have found that metakaolin-based geopolymers are obtained by calcination for about 2 to 6 hours at temperatures ranging from 500 °C to 750 °C [58]. Some researchers use metakaolin as an ideal feedstock for the manufacture of geopolymers because of its high reactivity and purity compared to other clays. Na$_2$SiO$_3$ activated geopolymers without CHT additives showed a lower leach percentage of about 10-18% SeO$_3^{2-}$ and SeO$_4^{2-}$ while NaOH activated geopolymers were around 58-74% [69]. The geopolymerization process using the isothermal calorimetric technique with the alkali-metakaolin
system identified the optimum temperature at 60 °C presenting the best physical and mechanical properties [70]. Magnetic geopolymers can adsorb 94% acid red 97 dye for 20 minutes and adsorption capacity of 1814 mg/g using Henry's isotherm model [15]. The geopolymer product with a sol-gel condensation reaction between sodium aluminate and sodium silicate dissolved in an alkaline solution shows the typical geopolymer characteristics similar to natural metakaolin [71]. The ion exchange geopolymer based on metakaolin which was synthesized at 40 and 90 °C with and without NH₄Cl solution showed that TiO₂ nanoparticles appeared micro-pore geopolymers to adsorb MB [21]. In a single layer AG16 at the maximum absorption capacity of MGP was achieved for values higher than 100 mg/g. MGP presents an adsorption capacity of 400 mg/g and a removal percentage of 98.5% [72]. Natural sources of Al and Si have been used for geopolymer synthesis by the sol-gel method used to synthesize and purify Al₂O₃-2SiO₂ powder from aluminum nitrate ninehydrate and tetraethoxysilane as starting materials. The steric entrapment method has succeeded in making synthetic metakaolin, which involves aluminum nitrate nonhydrate Al(NO₃)₃-9H₂O, sol-SiO₂, and polyvinyl alcohol PVA for geopolymer synthesis. Experimental studies have shown that synthetic metakaolin works well for geopolymer synthesis [73].

2.4 Dolomite
Calcium carbonate and calcium-magnesium carbonate in the form of limestone, dolomite, marl, lime, and oyster shells are among the most widely used non-metallic materials in the industrial world. Dolomite is usually used by farmers called agricultural lime to reduce soil acidity and to balance the lack of magnesium, dolomite is physically easily destroyed because it is very fine [74]. Other silica-containing materials such as dolomite, perlite, and glass have been proposed for dye removal. Burnt dolomite has a higher equilibrium capacity to remove reactive dyes than activated carbon. It is inexpensive and only available in a few countries. It is a good adsorbent for decontamination use [75]. Batch kinetic data from experimental investigations of the removal of reactive dyes from aqueous solutions using thermally charred dolomite have been well described by empirical models of external mass transfer and intra-particle diffusion. It was found that external mass transfer and intra-particle diffusion had a rate-limiting effect on the removal process. This is due to the relatively simple macropore structure of the charred dolomite particles [47].

2.5 Biomass ash
The biomass ash used as a geopolymer raw material for dye adsorbents includes rice husk ash. Hydrothermally synthesized rice husk ash (RHA) based geopolymers were used for adsorption of methylene blue [76]. The addition of soybean oil to synthesize RHA-based geopolymers is superior to adsorbing MV10B dyes because it produces intrinsic pore properties compared to geopolymers synthesized without oil [77]. The adsorption capacity of 276.9 mg/g for 10 B methyl violet, mesoporous structure increases surface area, pore size, and pore volume was increased by metakaolin-based mesoporous geopolymers and rice husk ash synthesized with soybean oil [77].

2.6 Slag
Activated slag-based geopolymers (GASG) are a new type of nanocomposite and ZnO-loaded GASG synthesized and their microstructure, optical properties, photocatalytic reduction of hydrogen production, and oxidation degradation of dye wastewater were studied. When loading is low, ZnO in the amorphous form is spread over the surface of GASG. The UV-vis diffuse reflectance spectrum shows that the absorption edge for all ZnO/GASG nanocomposites underwent a blue shift compared to pure ZnO due to quantum size effects [46]. The GR/ASG1 photocatalyst showed the highest degradation efficiency and approached 91.16% for 110 minutes. Nanocomposites are synthesized by the reaction of two-dimensional graphene and nets such as alkaline-activated blast furnace based slag geopolymers and used as new photocatalysts for the degradation of methyl violet following second-order kinetics [78]. Geopolymer photocatalyst prepared using cementitious blast furnace (ASCM) activated granulation blast furnace with alkaline Fe₂O₃ by simple polymerization, ion exchange and
impregnation processes showed 100% degradation of congo red (CR) dye under UV irradiation. The highest dye degradation efficiency of 100% was obtained with 0.4 grams of geopolymer at an initial dye concentration of 6 mg/L under UV irradiation in 100 minutes by adsorption and hydroxyl free radical oxidation reaction. The surface area of 465 m$^2$/g due to the acid treatment can be seen from the BET characterization, the more suitable adsorption kinetics which are second-order kinetic, Langmuir adsorption model and shows single layer adsorption [79]. Table 1 presented the results of various studies reported on the effect of geopolymer adsorbent feedstock on adsorption capacity.

3. **Comparison of absorption of various geopolymers**

In general, a geopolymer adsorbent suitable for dye adsorption must meet the requirements, where the adsorbent has a surface that can absorb dyes, high adsorption capacity is tolerant of various wastewater parameters. Therefore, it is known that adsorbents from different raw materials with different treatments can provide different absorption capabilities.

Adsorbent based on fly ash which was activated by alkaline solution resulted in a pore size of 2.5080 m$^2$/g, a pore volume of 0.001567 m$^3$/g, a pore size of 1.1738 nm with a contact temperature of 25 °C so that it could adsorb MB dye with an adsorption capacity of 43.47 mg/g [65]. Geopolymers modified by soybean oil can increase pores, it is proven that the geopolymer based on fly ash and rice husk ash [77] produces a surface area of 62 m$^2$/g, a pore size of 14.3 nm and a pore volume of 0.36 cm$^3$/g for removes methyl violet 10B dye with an adsorption capacity of 276.9 mg/g. Metakaolin-based geopolymers activated with acid can produce a maximum BET surface area of 257.8 m$^2$/g with a temperature of 20 °C for 30 minutes to remove MB dye with an adsorption capacity of 101.5 mg/g [80]. Magnetic geopolymer that has been activated by metakaolin and silica to adsorb Red 97 has a surface area value with the BET method is 42.92 m$^2$/g. The average pore size was 4.88 nm and 0.0523 cm$^3$/g with an adsorption capacity of 1814 mg/g [15]. The surface of the pore particles measuring 387nm on the geopolymer synthesized with alkaline activated fly ash, the degradation efficiency reached 92.97% under UV radiation with an adsorption capacity of 0.696 mg/g, in contrast, to fly ash without UV radiation the adsorption capacity is only 0.669 mg/g [33].

4. **Comparison with other adsorbents**

Floatable and permeable geopolymer blocks prepared using fly ash, sodium hydroxide, hydrogen peroxide, and oleic acid showed an adsorption capacity of 50.7 mg/g for MB dye from wastewater with an adsorbent dose of 0.4 g in 48 hours. Geopolymer block added with H$_2$O$_2$ and oleic acid resulted in a larger pore surface area and pore volume, namely 67.62 m$^2$/g and 0.16 cm$^3$/g [86]. KOH can produce a surface area of 600 m$^2$ with a diameter of 2.11 nm and 0.32 cm$^3$/g in the mean volume of the pores to adsorb MB. Microwave-hydrothermal processed grape skins can produce a maximum adsorption capacity of 216 mg/g, with an operating time of 3 minutes and a temperature of 180 °C for this hydrothermal process [87]. Calcined sawdust can adsorb MB with an adsorption capacity of 416.7 mg/g at 30 °C, 526.3 mg/g at 40 °C and 819.7 mg/g at 50 °C [17].
Table 1. The results of various studies on the effect of geopolymer adsorbent feedstock with adsorption capacity.

| Adsorption dyes     | Raw materials          | Adsorption capacity (mg/g) | References |
|---------------------|------------------------|----------------------------|------------|
| Thionine            | Fly ash                | 0.008                      | [7]        |
| Safranine T         | Fly ash                | 0.006                      | [7]        |
| Methylene blue      | Fly ash                | 43.47                      | [65]       |
|                     | Fly ash                | 79.9                       | [41]       |
|                     | Fly ash                | 15.4                       | [5]        |
|                     | Fly ash                | 37.04                      | [64]       |
|                     | Fly ash                | 15.4                       | [42]       |
|                     | Kaolin                 | 101.5                      | [80]       |
|                     | Kaolin                 | 30.8                       | [68]       |
|                     | Kaolin                 | 111                        | [81]       |
| Acid-activated kaolin (AAK) | Fly ash with UV          | 50.2                       | [82]       |
|                     | Fly ash without UV     | 0.669                      | [33]       |
|                     | Fly ash                | 0.696                      | [33]       |
|                     | Fly ash                | 37.04                      | [23]       |
|                     | Metakaolin GP          | 43.48                      | [23]       |
|                     | Metakaolin based GP    | 3.0                        | [10]       |
|                     | Metakaolin GP          | 3.2489                     | [83]       |
| Cu2O/TiO2-CTAB GP   | Fly ash                | 19.7                       | [84]       |
| Malachite Green     | Fly ash                | 233.30                     | [40]       |
|                     | kaolin                 | 128                        | [85]       |
| Rhodamin 6G         | Fly ash                | 381.70                     | [40]       |
|                     | kaolin                 | 46.08                      | [11]       |
| Rhodamin B          | Coal Gangue            | 1.035                      | [57]       |
| Eosin dye           | Raw coal fly ash (RFA) | 43.48                      | [39]       |
|                     | Powder (PCA)           | 62.28                      | [39]       |
| Methyl Orange       | Kaolin                 | 1.247                      | [66]       |
|                     | Metakaolin             | 3.076                      | [66]       |
|                     | Activated (GEO-7)      | 0.3393                     | [66]       |
| Acid Red 97         | Metakaolin             | 1814                       | [15]       |
| Methyl violet 10B   | Fly ash                | 276.9                      | [77]       |

5. Conclusion
This paper examines the progress and challenges in the use of geopolymers for the adsorption of dyes in wastewater. Geopolymers have shown excellent performance in removing dyes with a variety of geopolymer base materials, not eliminating their performance as adsorbents. Fly ash, kaolin, and metakaolin currently dominate geopolymer base materials which are most widely used to remove dyes from liquid waste. Geopolymers can be comparable to other adsorbents in that their application needs to be extended to other water and wastewater pollutants such as pharmaceuticals, oils and fats, phenolic compounds, micro-pollutants, and others. For future challenges, geopolymers must be tested in more depth with other feedstocks that can be the embryo of geopolymers at an economical cost and produce no residue, geopolymers must be tested in real wastewater with a multi-component system in a sustainable operation.
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