A Review of Geopolymer Based Metakaolin Membrane as an Effective Adsorbent for Waste Water Treatment.

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Abstract. Geopolymer-based products help eco-accommodating sources of materials such as metakaolin, slag or fly ash. This review explores the blend configuration to generate geopolymer-based metakaolin membrane metakaolin and to evaluate the impact of a range of geopolymer-based metakaolin sintering temperatures at a temperature of 50 °C, 60 °C, 70 °C and 80 °C. As the quick development of a modern culture contributes to a large increase in interest in water, adsorption is taken closer to examined waste water extraction of the adsorption and repulsion of a metakaolin membrane geopolymer. Membrane waste water treatment is chosen to explore simple and inorganic membrane preparation techniques that have long help lives and low production costs. Reviews for geopolymer-based metakaolin membrane were therefore synthesized via a suspension that depends on the quick solidification method of high temperature suspension geopolymer slurries that were used as an adsorbent for treating waste water. Porous geopolymeric spheres have developed a homogenous structure with the aid of electron microscopy and Brunauer-Emmett-Teller (BET) investigations. Since permeable materials are regularly adsorbents, this examination has analyzed the adsorption by membrane geopolymers of heavy metals. This finding will advance the formation of improved wastewater treatment systems and along these lines give an elective answer for ecological harm brought about by substantial metal contaminations. Along these lines, molar (SiO₂/Na₂O) ratio of metakaolin and sodium silicate are fundamental in assembling a sort of geopolymer-based inorganic membrane which does not require a high temperature sintering process. Adsorption and dismissal consolidated can be utilized for wastewater auxiliary electrical plating forms not exclusively to proficiently wipe out center and low groupings of overwhelming metals in wastewater yet in addition to wipe out little sub-atomic contaminants in wastewater.

1. Introduction
A sort of metakaolin-membrane geopolymer has been integrated by a suspension that depends on the speedy solidifying instrument of high-temperature geopolymer slurries. Sodium hydroxide and sodium silicate are the most generally utilized for geopolymers. In the light of the most recent research, the most soluble activator for geopolymerization will be to use sodium hydroxide with a sodium silicate solution [1].

A non-cristalline geopolymer with a three-dimensional aluminosilicate network structure proposed by Davidovits [2-4] is an alternate environmental resource. The high performance, low shrinkage, acid
tolerance, thermal stability, efficient solidification and the low cost of such products has recently shown very significant commercial and technological potential, but such properties are rarely recorded in membrane materials [5-8]. Geopolymeric products have shown significant commercial and technological potential. Geopolymeric aluminosilicate materials are a type of cross-connected long chain inorganic polymeric material, which has excellent high strength, anti-corrosion, fireproof and long-life characteristics between tetrahedral (AlO₄) [SiO₄] units [9]. Geopolymers are amorphous gels with porous structures, which also act as adsorbents that allow them to trap heavy metal ions[10].

This can better be used in other experiments as immobilization of heavy-metal ions [5, 9]. Recent years, geopolymers as adsorbents have been seen to absorb heavy metal ions from aqueous solution, and the versatile porosity and adsorption potential of geopolymers has been shown [10-13]. For this analysis geopolymers were synthesized by different conventional methods such as powders, characterized by XRD, BET and pore size distribution, adsorbent dosage structure, initial concentrations and pH.

As a result of the exponential development of an urban population, the need for water is considerably greater, this analysis research is focused on a wide range of advantages, including easy cycling, no changing phases, energy efficiency, low pollution and ongoing operation[14].

2. Materials and Method

2.1. Preparation of Raw Materials
The metakaolin was collected from 2 hours kaolin calcination at 800 °C [13, 14]. The used kaolin was purchased by Allied Kaolin Industries Sdn. Bhd. Malaysia. The actual structure of the kaolin used was powder form which contained at least 40% less than 2 μm in scale which average 2% in moisture density. South Pacific Chemical Industries Sdn. Bhd. (SCPI), Malaysia supplied the Na₂SiO₃ technological grade oil with 30.1% SiO₂, 9.4% Na₂O, and 60.5% H₂O composition (SiO₂/Na₂O ratio of 3.20). The Na₂SiO₃ fluid is colorless and can quickly be dissolved in water. NaOH has been extracted from the Formosoda-P stock, supplied to 99 % by Formosa Plastic Company in Taiwan. 10M NaOH was made with purified water by dissolving the NaOH pallet [15-17]. After it was dissolved with distilled water, NaOH was permitted to cool for 24 hours at room temperature. Chemical company provided hydrogen peroxide, PEG-600 and polysorbate 80 as surfactants. Cu(II) was set up in refined water by dissolving the Cu(NO₃)₂; Pb(II) particle stock arrangement was set up by disintegration of Pb(NO₃)₂ in refined water; Ni²⁺ ion stock solution was framed by dissolving Ni(NO₃)₂•3H₂O into distillated water and the Ca²⁺ particle stock solution was set up by dissolving CaCl₂ in refined water, and this arrangement was weakened to acquire the focus required for the examination.

2.2. Characterizations
For the study of morphology, a Hitachi electron microscope with a speed of 10kV was used. The crystalline composition of structures with X-ray diffraction has been studied in Rigaku D/MAX2500v. Standard monitoring of the BET surface region has been carried out. Appropriations of size are solved from desorption separates of BJH-based isotherms. An electronic porosimeter for mercury destruction calculated the total porosity. Last but not least, ion concentration measured by optical spectrometry.

2.3. Preparation of Metakaolin Membrane based Geopolymer
Metakaolin membrane geopolymer is gotten by a suspension and solidification process appeared in Figure 1. The strategy for the hardening of geopolymeric circles was an outcome of the quick solidification of geopolymeric paste at a high temperature of 80 °C, as different past investigations have just demonstrated [13]. The geopolymeric circles were easily set in the water bath.
2.3.1. Preparation of the slurry
NaOH was dissolved in a SiO$_2$/Na$_2$O molar silicate ratio = 0.5, 1.0, 1.5 and 2.0 [17] Metakaolin powder are then applied to the Na$_2$O/Al$_2$O$_3$ alkaline solution with a molar proportion of 1.0, 1.2, 1.4, 1.6 and 1.8 [14, 15]. These blending parameters researched the impact of mixing proportions for the production of a metakaolin layer geopolymer. It followed by adding hydrogen peroxide, H$_2$O$_2$ and Polysorbate 80 as surfactants in watery solution. H$_2$O$_2$ and Polysorbate 80 were 1.5% and 0.5% separately individually [15]. To get foamed slurry, the mixture was blended.

2.3.2. Preparation of the geopolymeric sphere
The homogeneous slurry is constantly injection in a 70 °C water bath PEG-600 solution using syringes to prepare the microbeads of porous geopolymers. The beads suspended and dissipated as spheres in the PEG-600 medium and can solidify and float at high temperatures instantly. The densities of geopolymer beads and PEG-600 were around equivalent under surface strain impacts. So as to evacuate the overabundance sodium hydroxide, the circles could then be effortlessly gathered. This analysis also evaluates the influence of various geopolymer-based metakaolin membranes sintering temperatures. The porous geopolymeric spheres were therefore obtained for 24 hours after drying at an elevated temperature of 50 °C, 60 °C, 70 °C and 80 °C [18-21]. Unfoamed geopolymer was also developed as a guide in the development, perhaps without moisture agents.

![Figure 1. Suspension solidification of geopolymeric spheres](image)

2.4. Adsorption Test
This study carried out a series of adsorption tests to analyse heavy metal adsorption mechanisms which affect the effectiveness of geopolymers with different parameters. This work performed two main studies as follows: (1) adsorption testing for heavy metal removal from aqueous solutions, consisting of results on various ratios of solid to aqueous solution for geopolymer adsorption; and (2) elute sample desorption tests collected from the first experiment, which included examining the desorption properties of heavy metals by geopolymer. Whether combined with an aqueous solution containing heavy metals, the powerful alkaline geopolymer induces precipitation by the hydroxide reaction. To prevent adsorption damage, strong geopolymer samples were washed in 60 °C DI water for 1 hour at 30 rpm and then steam washed for 24 hours. Until filtration and drying, the samples were washed by DI water multiple times until at least 24 hours of washing water pH was preserved at 7±0.5 [5]. Adsorption tests were undertaken with the washed geopolymer as an absorber and heavy metal vapor. Pb$^{2+}$, Cu$^{2+}$, Ni$^{2+}$ and Ca$^{2+}$ have been prepared primarily from regular analytical solutions. For through adsorption examination, the original pH of the
overwhelming metal structure was below pH 5. The supernatant reaction fluid was isolated by centrifugation following adsorption and gathered for additional examination.

2.4.1. Effect of Ph
The blank solutions 50 mg/L Pb²⁺, Cu²⁺, Ni²⁺ and Ca²⁺ have been formulated at various pH values of 2.0, 3.0, 4.0 and 5.0 by modification at all 0.1 M HNO₃ and 0.1 M NaOH. 100ml of 50 mg/L Pb²⁺, Cu²⁺, Ni²⁺ and Ca²⁺ have been approached at specific pH rates with a steady adsorbent concentration of 0.15 g for 48 hours.

2.4.2. Effect of initial concentration of heavy metals solutions
In addition, 0.15 g of adsorbents have been applied to 100 mL solutions at varying concentrations of Pb²⁺, Cu²⁺, Ni²⁺ and Ca²⁺ (10–120 mg / L). The interface time was 48 hours at 25 °C for perfect equilibrium. The adsorption capacity, (Qe) geopolymer sphere adsorbents was evaluated by calculation at selected times and then using the following equation of metal ion concentration changes:

\[ Q_e = \frac{V(c_0-c_e)}{m} \]  

Where the original and final metal ion concentrations are C₀ and Cₑ (mg/L) respectively, the solution capacity is V (L) and the geopolymer dosage is m (g).

3. Results and Discussions
3.1. Synthesis of porous geopolymer spheres
By suspension solidification, permeable geopolymer circles were acquired, as found in Figure 1. This procedure was separated into two segments, as expressed. Firstly, the slurry arranged has been gotten. The most grounded result originates from the disintegration of 13.22 g NaOH in a 10000 g sodium silicate solution with 1.6 SiO₂/Na₂O molar proportion[11] at a 10 M NaOH concentration. This can be because of the upgraded disintegration of the metakaolinite particles and, consequently, to the force of the monomer condensation within the sight of higher NaOH [22]. In this alkaline solution 24.38 g Metakaolin powders, 15.00 g were subsequently applied at a molar ratio of Na₂O/Al₂O₃ = 1. Instead the foaming agent, 0.59 g was added to aqueous solutions (H₂O₂ = 1.5 %). The molar ratio of H₂O / Na₂O = 16 was applied to the 4.15 g purified water. Finally, to receive foamed slurry, the mixture was mixed. Secondly, the high surface tension geopolymer slurry was used for the preparation of porous geopolymer spheres. The homogeneous slurry was continuously injected into the PEG-600 matrix, utilizing syringes to prepare porous geopolymer micro beads, at water bath temperature of 70 °C. The micro beads were suspended and scattered all through the medium PEG-600 as spheres, which effortlessly set and floated at high temperatures. The circles were immediately separated and afterward cleared out of sodium hydroxide with refined water. After vacuum drying for 24 hours at 60 °C and room-hardening for 3 days, permeable geopolymer spheres were acquired 2–4 mm in diameter[11]. The foamed geopolymer paste was utilized as an apparatus for estimating time.

3.2. Preparation mechanism of geopolymer spheres
In general geopolymerisation involves four steps [13, 14]: (1) dissolution in the heavy alkaline aqueous solutions of solid aluminosilicate materials; (2) creation of a paste comprising Si- and/ or Si-Al oligomers; (3) polycondensation by a paste to the inorganic polymer gel after elimination of water molecules; and (4) binding the undissoosed organisms into a paste. The amount of foaming agent present during the reaction was limited while preparing porous geopolymer spheres. While the H₂O₂ surfactant promotes spherical shape forming in the suspension, it simultaneously decreases geopolymerization [15, 16]. The geopolymer foam paste polycondensation method then demonstrated
traditional geopolymerisation properties. Stages (3) and (4) are essential to solidify geopolymer circles. The suspension liquid can easily solidify and align the geopolymer circles while retaining the geopolymer foam paste more noteworthy. PEG-600 is a reasonable dissolvable for this application as the essential gravity is 1.128 g/cm³ and adequate hydrophilicity. The flash point is likewise more notable than 230 °C, and it may well can be utilizes comfortably throughout the process of suspension solidification. Impacted by the quick solidification of the geopolymer paste in high-temperature suspensions, the hardening system of the geopolymer circles is known beforehand [23, 24]. Figure 2 shows the normal beginning setting period of geopolymer froth slurries subject to metakaolin as a part of the rising temperature. The initial setting period decreased with the increased curing speed. The geopolymer slurry initial setting period was 92 minutes at 40 °C. The geopolymer slurry was however solidified in 17 minutes by an increase of 70 °C in the curing temperature. This finding shows that increasing the curing temperature would speed up the processes of polymerization and solidification in the geopolymer paste [23-26].

Figure 2. Original configuration of geopolymer foam slurries at various temperatures [27]

The results revealed that the solidified geopolymer paste was around 1.0 g/cm³ in mass density after 5 minutes in the laboratory conditions found inside it. The bulk densities of the relieved geopolymer balls diminished to 0.79 g/cm³ subsequent having dried under a vacuum at 60 °C for 24 hours. Geopolymerization is isolated from other conventional processes in a polyethylene glycol medium [22, 23]. The solution polyethylene glycol was therefore selected as a matrix to strengthen the suspension. The dynamic density of the solution can be changed by inserting multi ethylene glycol with different molecular weights. The last suspension method for geopolymer sphere blend was chosen for polyethylene glycol (PEG) arrangement with a molecular weight of 600 based on the findings of an enormous number of studies [28, 29].

3.3. Structure characterization and analysis
Figure 3(a) and (b) are seen as SEM micrographs of the geopolymer spheres. The adsorbent had a distinct porous composition, consisting of many layers that were capable of supplying fluid penetration channels and a strong adsorption surface. The geopolymer spheres SEM micrograph was seen in the figure following an adsorption cycle on Cu (II) objected in Figure 3(d).
Figure 3. SEM images: (a) the exterior surface, (b) the transparent microstructure; (c) the outer surface of the spheres without applying H$_2$O$_2$, (d) the pore microstructure following adsorption on Cu(II)[30]

The XRD was used to analyze kaolinites, metakaoline and geopolymer. Figure 4 shows that the geopolymer structure was not crystalline.

Figure 4. The XRD analysis included kaolinite, metakaolin and geopolymer. [5]

In geopolymeric spheres, the BET specific area as determined by N$_2$ gas adsorption was 53.95 m$^2$/g. As shown in Fig. 3 (c) and BET-specific surface area of 9.56 m$^2$/g, the geopolymer sphere was dense without introducing H$_2$O$_2$. The wide area can be associated with metal ions with the aid of H$_2$O$_2$ and various active sites. The mesoporous and micro-porous composition of the geopolymer spheres must be defined by an automated mercury intrusion porosimeter examination. Regarding geopolymeric spheres combined quantities of penetration and unequal intruding pore volumes as seen in Figure 5. The sphere pore depth was 0.006 μm to 200 μm in height. The pores of the geopolymeric spheres are localized primarily at about 15 nm, suggesting the presence of significant amounts of mesopores in the spheres (2 nm < pore diameter < 50 nm). The pores of the porous spheres of the Geopolymer were 1.29 cm$^3$/g and 0.79 g/cm$^3$, with a minimum porosity of 60.30%.
3.4. Adsorption test

In 100 mg/L of Cu (II) solution, a 1.5 g/L portion of geopolymer adsorbents has been applied at pH 5. Figure 6 shows discoveries for 72 hours ionic corrosive exposures. The entirety of adsorbed Cu (II) expanded with developing contact time and arrived at adsorption equilibrium following 36–50 hours, around 34.5 mg/g $Q_e$. As the contact time rose from 50 hours to 60 hours, $Q_e$ stood at about 35.5 mg/g. This finding suggested that a contact time of approximately 50 hours may be sufficient for adsorption conditions of equilibrium. Under a similar adsorption conditions, the volume of adsorbed Pb (II) expanded with contact time, accomplishing equilibrium following 36–50 hours and a $Q_e$ of about 45.1 mg/g. With the contact time frame ascending from 50 hours to 60 hours, $Q_e$ remained stable at around 45.6 mg/g. This outcome demonstrated, nonetheless, that the adsorption pace of Pb (II) was quicker than the adsorption pace of the Cu (II) term of 36–50 hours to arrive at equilibrium in adsorption conditions. Besides, contact time for adsorbed $Ca^{2+}$ was expanded in equilibrium following 50–60 hours, with an adsorption of 24 mg/g $Q_e$ being equivalent. The contact time of 50–60 hours is satisfactory in equilibrium conditions however the $Ca^{2+}$ adsorption rate is weaker than Cu (II) and Pb (II) respectively.
An essential parameter for adsorption strength is the aqueous pH solution. The adsorbent surface burden, the metallic particle hydroplets complexes, the ionization level and speciation adsorbate in response are significantly influenced by this adsorbent factor[21, 22]. In the current study, heavy metal solution pH increased incrementally from 2 to 5 to assess its impact on adsorption efficacy, as shown in Figure 7. Experimental results indicated an increase in solution pH in conjunction with the geopolymer heavy metal adsorption capacity.

Figure 7. Original pH on heavy metal adsorption [3]

The volume of heavy metals adsorbed increased with the solution pH increased. The key explanation is that when H⁺ becomes higher in the solution, the adsorbent prefers to use H⁺ for adsorption. Consequently, heavy metals adsorption ability reduces in a lower pH [32, 33].

4. Conclusions

The present research demonstrates the efficient synthesis by suspension solidification of porous metakaolin-based geopolymorphic spheres. A fast solidification of geopolymers paste in high-temperature suspensions is the foundation for the solidification of the spheres. The geopolymer dependent on metakaolin with a SiO₂/Na₂O molar ratio of 1.0 alkaline solution is of outstanding adsorption efficiency. SEM and pore-sized diffusion experiments clearly showed the rigid nature of the geopolymeric spheres. The tests revealed that the geopolymer circles were permeable with various mesopores. The findings demonstrate that the geopolymer adsorption reaction for substantial metal particles is an endothermic response and indicates an ionic response because abundant metal particles obey Na⁺ in the geopolymer. Furthermore, the measure of overwhelming metal particles adsorbed to the geopolymer can increment by a higher pH (for instance, pH 4–5). Testing for adsorption and desorption have showed the excellent removal efficiency of porous geopolymer spheres for Cu²⁺, Pb²⁺, Ni²⁺ or Ca²⁺ and can be used as an adsorbent for appropriate metal ion adsorption. The particle adsorption process on the geopolymer circle was involved compound and physical adsorption after the adsorption energy of Cu²⁺ was examined. The metakaolin layer comprising of permeable geopolymeric territories is not only inexpensive, simple and ecologically protected, yet has solid capacity to dispense with overwhelming metal particles from the treatment of waste water.

Acknowledgments

The author would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under a grant number of FRGS/1/2019/TK.10/UNIMAP/02/21 from the ministry of Education Malaysia.
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