Application of Geopolymers in Adsorption

Subjects: Materials Science, Ceramics

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Geopolymer is a porous inorganic material with a three-dimensional mesh structure, good mechanical properties, a simple preparation process (no sintering) and a low economic cost, and it is environmentally friendly. Geopolymer concrete has been widely used in the construction field, and many other studies have revealed that geopolymer will become one of the most promising inorganic materials with unique structure and properties. Geopolymer has a three-dimensional mesh structure that provides the geopolymer with high porosity and a significant number of mesopores that enhance the adsorption capacity by providing more exposed binding sites on the surface. The high mesoporous structure, high porosity, and three-dimensional mesh structure give geopolymers a larger specific surface area, which increases the contact sites with pollutants and impurities.

Keywords: geopolymers ; adsorption ; heavy metals ; dyes

1. Introduction

Research on the preparation of new environmentally friendly materials using fly ash, metakaolin, and other substances containing large amounts of silicon and aluminum elements as raw materials has become highly popular in recent years. These materials will be processed to produce innovative materials with amorphous and quasi-crystalline three-dimensional mesh structures. This relatively inventive material is referred to as Geopolymer, which was originally conceived by French scientist Joseph Davidovits in 1978 [1][2]. Davidovits [3] prepared for the first time new inorganic silica–alumina gel materials with a three-dimensional structure using the reaction of alkaline solution NaOH/KOH with metakaolin. Developments in geopolymers are not only naturally occurring silicate mineral polymers, but the concept also includes natural minerals, slag, industrial waste, volcanic ash, and solid waste to produce gel polymeric materials with amorphous and quasi-crystalline structures [4][5][6].

With the continuous development of modern technology, porous geopolymers have attracted significant attention from academia and industry under their unique three-dimensional structure. Geopolymer products have stable chemical properties, thermal stability, inexpensive and accessible raw materials, and a simple preparation process [7][8][9][10][11]. The geopolymer has excellent practical applications when used as a modern green inorganic porous material. This area is surrounded by extensive research directions. The microstructure of geopolymers has more irregular pores with larger specific surface areas and the three-dimensional mesh structure is favorable for capturing adsorbed substances.

Adsorption is a mass transfer process in which a substance is transferred from one phase to another. According to the different forces of attraction between substances, they could be divided into chemisorption and physical adsorption. Contaminants accumulate on the adsorbent surface due to physical forces such as van der Waals forces, hydrogen bonding, hydrophobic interactions, polarity and space forces. The dipole-induced dipole interactions and the chemistry of π–π interactions also produce adsorption effects [12]. Adsorption could be used for purification, decolorization, separation, deodorization, concentration, and detoxification, and it is becoming increasingly important in many areas of production [13]. There are various adsorption materials, and the commonly used inorganic adsorption materials are silica gel, activated alumina, zeolite, etc. Organic adsorbents are polyacrylamide, resin, cellulose, etc. Adsorption as a highly efficient means of pollutant removal technology has received much attention, where adsorption materials directly affect the adsorption effect, and efficient green adsorption materials have become a popular research subject. Researchers have found that nanomaterials exhibit high adsorption capacity for pollutants such as dyes, heavy metal ions, etc. [14][15][16]. With the advancement of technology, new types of adsorbent materials have been reported for the adsorption of pollutants, such as spinel ferrite magnetic materials, nanomagnetite-modified biochar, ligand-immobilized facial composite adsorbent, mesoporous adsorbent, graphene-based adsorbents and agro-industrial waste derived adsorbents [17][18][19][20][21].

Adsorbent materials are green and safe, economical and low-cost, easy-to-recycle, and abundant raw materials. Adsorbent materials may be prepared from minerals, shellfish, starch, tree bark, industrial and agricultural wastes, etc.

Adsorbent materials could treat a variety of pollutants such as heavy metal ions, dyes, organic matter, and CO_2 [22]. Adsorption is possible in combination with other technologies and photocatalytic technology to increase the adsorption capacity while improving the efficiency of dye degradation [23].

2. Heavy Metal

Water sources in several worldwide suffer from heavy metal pollution, while geopolymers with their strong ion exchange capacity [24][25] and three-dimensional structure become potential materials for heavy metal adsorption. The preparation of adsorbent materials using geopolymers as source material for research on adsorption/immobilization of metal ions has been carried out extensively until now. The adsorption experiments of Cu^{2+} using fly ash and iron ore tailing to synthesize porous amorphous geopolymer revealed a total porosity of 74.6%. The uptake capacity reached the highest value of 113.41 mg/g at 40 °C [26]. It is remarkable that when geopolymer is used as an adsorbent, pH has a significant effect on the adsorption capacity of most of the adsorbents, and pH regulation is often required to obtain the best adsorption effect. When the pH is low, the solution contains high amounts of H_3O^+, which competes with metal cations for the exposed active sites of porous geopolymers, resulting in a lower capacity to adsorb cations such as Cu^{2+}, Zn^{2+}, Pb^{2+}, etc. When the pH increases, H_3O^+ decreases, and the competition for metal cations becomes stronger. Take Cu^{2+} as an example, when the pH value is high, the OH^- concentration in water increases, and a large amount of OH^- generates $Cu(OH)_2$ precipitation with Cu^{2+}, resulting in poor adsorption performance. The maximum monolayer adsorption capacities were 72.3 mg/g and 69.2 mg/g for Mn^{2+} and Co^{2+} for the removal of Mn^{2+} and Co^{2+} heavy metal ions from aqueous solutions using metakaolin-based polymers. The adsorption efficiencies were observed to be slightly sensitive to temperature and ionic strength, but high adsorption rates could be obtained without pH adjustment [27].

The silicate category of materials itself also has certain adsorption properties. The fly ash, fly ash-based polymer and faujasite block were compared in the experiment and Pb^{2+} was used as the adsorption target. When pH = 3, the maximum adsorption capacities of fly ash, geopolymer and faujasite block were 49.8, 118.6 and 143.3 mg/g, respectively, indicating that the adsorption efficiency of geopolymer and faujasite block was much higher than that of fly ash, and the entropy difference in adsorption among the three indicated that fly ash was mainly physical adsorption of Pb^{2+}, while geopolymer and faujasite block are chemisorbed [28]. Metakaolin-based polymers were used as adsorbents for the removal of Zn^{2+} and Ni^{2+} ions from aqueous solutions, and the maximum monolayer adsorption capacities of Zn^{2+} and Ni^{2+} determined by Langmuir adsorption isotherms were 1.14×10^{-3} and 7.26×10^{-4} mol/g, respectively. Adsorption research in continuous mode demonstrated that the optimal flow rate was 2.0 mL/min for Zn^{2+} and 1.0 mL/min for Ni^{2+} [29].

Under the experimental conditions of continuous operation, it was discovered that besides the common influencing factors, namely, initial concentration of ions, amount of adsorbent, adsorption time, pH, etc., flow rate also affects the adsorption efficiency of the material. The geopolymers prepared at different alkali activator moduli (silica/sodium oxide = 0.8, 1.2, 1.6, 2.0 mol/L) using the same metakaolin raw material had different adsorption capacities when prepared with different alkali activator moduli agents. When the geopolymer prepared with alkali activator modulus of 0.8 mol/L showed the best adsorption performance for Cd^{2+}, the maximum adsorption capacity was 70.3 mg/g [30].

To improve the adsorption capacity and various properties of the adsorbent, the geopolymer could be modified and altered by adding other substances during the preparation of the geopolymer. Synthesis of innovative geopolymer–alginate–chitosan complexes using a mixture of metakaolin geopolymer and sodium alginate solution and chitosan for direct removal of Pb^{2+} from wastewater [31]. Hollow gangue microspheres were inserted into the geopolymer matrix by the geopolymer method for the removal of heavy metal ions (Cu^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+}) from aqueous solutions. The adsorption principle of this adsorbent material was attributed to physical, chemical, electrostatic attraction, and ion exchange by pseudo-second-order kinetic model fitting, equilibrium isotherm adsorption data and Langmuir equation fitting analysis in this experiment [32]. While silicates are generally used for geopolymers, other substances could be used to provide silica and aluminum sources for the preparation of geopolymer-based adsorbent materials. Some nano-zeolite and geopolymer/zeolite products could be synthesized at low cost by using rice husk and waste aluminum cans as silicon and aluminum sources, respectively, and the synthetic products could effectively remove Co^{2+}, Cu^{2+} and Zn^{2+} [33].

3. Other Ions

Geopolymer adsorbent materials could adsorb NH_4^+, anionic sodium dodecyl benzene sulfonate and other pollutants, in addition to common heavy metal ions. The geopolymer of metakaolin was made into granular form for the adsorption of NH_4^+. Experiments were conducted in municipal wastewater treatment plants on a pilot basis, and the NH_4^+ effluent concentration was always maintained at 4 mg/L at a water temperature of 10 °C [34]. The application of geopolymer adsorbent materials for NH_4^+ removal from waste leachate and NH_4^+ removal from piggery wastewater has also been investigated [35][36]. This indicates that the porous ground polymer particles have high selectivity for NH_4^+ even in the presence of organic compounds and competing ions [36]. The geopolymer adsorbent could capture the anionic surfactant sodium dodecyl benzene sulfonate, similarly to the above-mentioned adsorption process, which the adsorption is chemical and physical at the same time [37]. Cation exchange processes (Na^+ substitution by Ba^{2+}) occur in the framework structure of the geopolymer using Ba for geopolymer modification. The Ba-modified geopolymer materials exhibited higher adsorption rates for SO_4^{2-} in the pH range 7–8 [38].

Adsorption calculations by pseudo-second-order kinetics, Langmuir isotherm model, etc. suggested a uniform distribution of adsorption sites and the formation of a monolayer of adsorbate on the surface of the geopolymer in most of the adsorption processes. In several studies, heavy metal ions are better adsorbed under strongly acidic conditions because the solution contains more H^+ in strongly acidic conditions, which means that there is the higher free energy of hydration and could exchange metal ions more effectively [39]. The adsorption capacity is not limited to the adsorbent material itself but is determined by the experimental conditions. Different experimental conditions have to be explored for different ions in return for the best adsorption effect.

4. Dyes

In research on the extraction of methylene blue from synthetic wastewater by fly ash-based geopolymer spheres, the removal efficiency of methylene blue uptake reached 79.7 mg/g and remained up to 83% after eight cycles of regeneration. The surface of the spheres is smooth and the large number of pores inside the spheres, and the open small pores on the closed macropores expose more active sites to improve the adsorption. Additionally, the significant difference in chemical elements between two parts of the spheres was found by EDS, which was caused by the inhomogeneity of the particles and the chemical differences in the precursors [40].

The geopolymer balls could be prepared by liquid nitrogen drop technique, in which PEG600 is added as a binder to adsorb methylene blue, and the removal efficiency of all beads after 24 h reaches 98% removal on average. The efficiency observed is mainly associated with the morphology and porosity of the beads, which in turn is directly related to the water content added to the geopolymer slurry [41]. Other research on the adsorption of methylene blue has demonstrated that this adsorption method is effective and feasible, and is expected to be used directly in industrial wastewater treatment in the future [34][42][43]. These fly ash-derived inorganic polymers also exhibit excellent adsorption properties when adsorbing crystalline violet from aqueous solutions [44]. Magnetic geopolymers were used as effective aqueous decolorization adsorbents for the removal of acid green (AG) and procion red (PR) from aqueous solutions. The results of the theoretical calculations of the bilayer adsorption model and the corresponding performance tests confirmed that the active sites of the magnetic ground polymers are favorable for binding to the smallest dye molecules, thus improving the adsorption capacity [45]. Simplified and low-cost surface modification of previously prepared fly ash-based polymers with cetyltrimethylammonium bromide (CTAB) was able to remove anionic acid blue 185 (AB185) without strong acid conditions, with a maximum removal efficiency of 98.2%, and this indicates that electrostatic interactions also have a major effect on the adsorption process [46]. The mesoporous geopolymer was synthesized using a new and simple synthesis method using metakaolin and rice husk ash as the source of silica and alumina, and the material was tested for the removal of methyl violet 10B (MV10B) from an aqueous solution. The results demonstrated that the maximum adsorption capacity of the mesoporous geopolymer was 276.9 mg/g, and that the adsorption was spontaneously generated with a heat absorption process [47]. With Rhodamine B as the removal target, using geopolymers as adsorbents, the removal capacity was increased as the contact time increased, allowing the active sites to interact more fully with the dye molecules. However, this experiment also showed that when the contact time exceeded a certain critical time, the adsorption capacity stopped increasing [48]. Activated geopolymer with a specific surface area of 35.7 m^2/g was used for the adsorption of methyl orange (MO) dye, but the experimental results showed that compared to kaolinite and metakaolinite, activated geopolymer had the largest specific surface area, but the adsorption effect was lower than the other two substances. This might be explained by the fact that MO is an anionic acid dye and the silicone bonds on the surface of geopolymer are negatively charged, MO and hydroxyl ions (OH^-) compete with each other at the adsorption sites [49].

Dye wastewater is expensive to treat because it contains a large amount of pigments and organic matter, while geopolymers possess the characteristics of low cost, green and high adsorption efficiency. The geopolymer adsorbent materials prepared at different temperatures all showed excellent adsorption performance in the treatment of dye wastewater, but geopolymers have poor adsorption performance for both negatively charged ions and anionic dyes, which is caused by the charge characteristics of the geopolymer surface. In a highly acidic environment, the surface of the silica–aluminate mesh of the geopolymer is protonated, thus becoming a positively charged adsorbent on the surface, which facilitates the adsorption of anionic dyes [50]. After modifying the pores, hydrophobicity of the material, surface charge and ionic affinity by adding suitable additives and changing the functional groups on the surface of geopolymers and their crystalline shape, it is expected to be used in large-scale industrial applications for the treatment of dye wastewater [51].

Absorption of heavy metals and dyes on geopolymers is mainly a spontaneous, heat-absorbing and entropy-driven process, and the adsorption process contains physical, chemisorption, and ion-exchange adsorption. Adsorption is frequently the result of the combined effect of three kinds of adsorption, which accounts for the major type of adsorption in the adsorption process as a result of differences in adsorbent substances, adsorption conditions, and adsorbents. Research in the future should focus on: improving the mechanical properties, adsorption performance and stability of geopolymer adsorbent materials; improving the adaptability of geopolymer adsorbent materials under different conditions, such as strong acidic and alkaline environments, organic–inorganic mixed solutions, high temperature and high pressure, and other complex environments; and studying the ability to adsorb pollutants other than heavy metals and dyes, and the application of continuous operation in practical wastewater [51].

5. Other Adsorption Applications

In recent years, research scholars have focused their attention on the application of geopolymers for gas adsorption. Cryogenic adsorption of CO_2 in solid materials is a highly cost-effective method for implementing decarbonization in retrofit plant strategies [52]. Selected alkali-based porous ceramic clay polymer materials applied to CO_2 adsorption exhibit excellent performance for better separation of CO_2/N_2 and CO_2/CH_4 gases [53]. To purpose of increasing CO_2 capacity, a novel composite material formed by embedding Na13X zeolite in a geopolymer matrix using K/Na silicate material as raw material. the CO_2 capacity of the Na^+-based composite is significantly greater than that of the K^+-based adsorbent (2–3 times) [54]. Simplifying the experimental procedure, a complex three-dimensional pore network NaX nano-zeolite-geopolymer monomer was finally obtained using a one-pot hydrothermal synthesis method, which has a BET-specific surface area of 350 m^2/g [55]. Practical production in industry produces CO_2 at high temperatures and mostly mixed gases, requiring adsorbent materials with high mass transfer, strong mechanical properties, great thermal stability and chemical stability. The talc-based powder was mixed with a metakaolin-based polymer matrix to prepare an innovative ground polymer-hydrotalcite composite material, which has excellent compressive strength at temperature and 500 °C while ensuring adsorption capacity, ranging from 10 to 35 MPa [56].

Geopolymers have been researched more in CO_2 gas adsorption, but the application of other gas adsorption has been less studied. The present studies suggest that geopolymer adsorbent materials with proper modification have high mass transfer, high stability and selective adsorption. They have great potential in the treatment of industrial waste gases, and their adsorption applications and adsorption principles for other industrial waste gases such as SO_2, CO, and H_2S could be explored in the future.

In addition to the common adsorption of heavy metals, dyes, and gases, geopolymers could be used for material separation using the principle of adsorption. The adsorption of formaldehyde in aqueous solutions using geopolymers, the cation exchange capacity of geopolymers is 2–3 times higher than that of natural zeolites, and the process of formaldehyde removal includes physical adsorption, chemical adsorption and complexation, which may be the reason for the stronger adsorption capacity of geopolymers for formaldehyde [57]. Experimental adsorption desulfurization of oil using geopolymers. The study revealed the presence of Na, Al, and strong acid sites on the surface of the prepared geopolymer. These sites interact with sulfur compounds in heavy gas oils through π–π and acid–base interactions [58].

6. Application of Geopolymer Membranes in Adsorption

Membrane technology has developed rapidly in recent years and is widely used for the separation, classification, purification or enrichment of multi-component liquids or gases. However, most of the mature membrane technologies used nowadays are organic membranes, which have the advantages of high treatment efficiency and easy operation, but have the disadvantages of high economic cost and serious membrane pollution. Inorganic membranes make up for the shortcomings of organic membranes, but inorganic membranes are more expensive to prepare, and the process is not mature. Therefore, the emergence of geopolymer membranes provides an opportunity for the development of inorganic membrane applications [59]. Numerous studies have proven that geopolymers have excellent adsorption properties, and the advantages of geopolymers could be exploited to prepare low-cost and high-efficiency inorganic membranes. Changing the form of a geopolymer used to make it renewable and reusable expands the scope of geopolymer applications in industrial production.

Biomass fly ash ground polymer monomers are used as adsorbents, and these monolithic adsorbents could be used as membranes after being used directly in filled beds [60]. Research has suggested that geopolymers could be prepared directly into membranes. The novel free-sintered self-supporting inorganic membrane simultaneously adsorbs and repels Ni^{2+} during the membrane separation process, which could effectively remove Ni^{2+} from wastewater while removing small molecule pollutants from water [61]. To increase the contact sites, improve removal efficiency, and facilitate use, geopolymers may also be prepared as tubular membranes. Porous gradient geopolymer-based tubular membranes were prepared using a one-step molding method for the removal of particulate matter (PM) [62].

The geopolymer membrane requires a higher compressive strength while having a greater specific surface area. Besides conventional fly ash or metakaolin, phosphate mine tailings could be used to produce geopolymer membranes, which also exhibit good compressive strength (11.2–43.7 MPa) and high BET surface area (321–384 m^2/g). The geopolymer membrane could effectively remove Cu^{2+} from water through the combined effect of ground adsorption and repulsion [63].

Appropriate modification of inorganic membranes could improve their adsorption capacity and mechanical strength. A metakaolin-based polymer composite membrane (support + dense layer) was prepared using metakaolin and alkali solution at lower temperature and atmospheric pressure, using porous ground polymer as a carrier and a dense layer on the surface using a double coating process. The composite membrane exhibited amorphous structure, high permeate water flux (245 kg/m^2·h), good interface combination and reusability. The membrane performs better on paper wastewater purification, effectively intercepting and adsorbing suspended solids in solution [64]. A new inorganic-organic composite membrane was prepared by electrostatic self-assembly method, choosing porous polymers as the carrier and using the “green” biomaterial chitosan to form the active layer. The effectiveness of the composite membrane in removing crystalline violet (CV) was attributed to the synergistic effect of repulsion and adsorption [65]. The porous zeolite ground polymer membrane (Geo) was used as the immobilization carrier to prepare laccase-immobilized ground polymer composite membrane for CV removal. CV molecules could be adsorbed on the porous Geo surface through the electrostatic attraction effect and van der Waals forces. Secondly, laccase is an oxidoreductase that could oxidize dye molecules, creating a synergistic effect between the two to achieve higher removal efficiency [66].

Geopolymer membranes are convenient to use compared to other forms of geopolymer-based materials and are reusable as they could be backwashed to restore the original flux. Modified and adapted geopolymer membranes have a variety of properties, and while acting as a carrier, the geopolymer membrane’s physical adsorption capacity help adsorb metal ions, resulting in higher removal efficiencies. The combination of geopolymers and other substances could maximize the synergistic effect and maximize the performance of the membrane material.

References

1. Davidovits, J. Geopolymers and geopolymeric materials. J. Therm. Anal. 1989, 35, 429–441.
2. Davidovits, J. Geopolymers: Man-made rock geosynthesis and the resulting development of very early high Strength Cement. J. Mater. Educ. 1994, 16, 91–139.
3. Davidovits, J. Recent progresses in concretes for nuclear waste and uranium waste containment. Concr. Int. 1994, 16, 53–58.
4. Bai, C.; Colombo, P. Processing, properties and applications of highly porous geopolymers: A review. Ceram. Int. 2018, 44, 16103–16118.
5. Yu, G.; Jia, Y. Preparation of geopolymer composites based on alkali excitation. Arab. J. Geosci. 2021, 14, 600.
6. Zhang, X.H.; Bai, C.Y.; Qiao, Y.J.; Wang, X.D.; Jia, D.C.; Li, H.Q.; Colombo, P. Porous geopolymer composites: A review. Compos. Part A Appl. Sci. Manuf. 2021, 150, 106629.
7. Amran, M.; Debbarma, S.; Ozbakkaloglu, T. Fly ash-based eco-friendly geopolymer concrete: A critical review of the long-term durability properties. Constr. Build. Mater. 2021, 270, 121857.
8. Komnitsas, K.; Zaharaki, D. Geopolymerisation: A review and prospects for the minerals industry. Miner. Eng. 2007, 20, 1261–1277.
9. Lahoti, M.; Tan, K.H.; Yang, E.H. A critical review of geopolymer properties for structural fire-resistance applications. Constr. Build. Mater. 2019, 221, 514–526.
10. Luhar, S.; Nicolaides, D.; Luhar, I. Fire resistance behaviour of geopolymer concrete: An overview. Buildings 2021, 11, 82.

11. Mesgari, S.; Akbarnezhad, A.; Xiao, J.Z. Recycled geopolymer aggregates as coarse aggregates for Portland cement concrete and geopolymer concrete: Effects on mechanical properties. Constr. Build. Mater. 2020, 236, 117571.

12. Saleh, T.A. Protocols for synthesis of nanomaterials, polymers, and green materials as adsorbents for water treatment technologies. Environ. Technol. Innov. 2021, 24, 101821.

13. Crini, G.; Lichtfouse, E.; Wilson, L.D.; Morin-Crini, N. Conventional and non-conventional adsorbents for wastewater treatment. Environ. Chem. Lett. 2018, 17, 195–213.

14. Tan, K.B.; Vakili, M.; Horri, B.A.; Poh, P.E.; Abdullah, A.Z.; Salamatinia, B. Adsorption of dyes by nanomaterials: Recent developments and adsorption mechanisms. Sep. Purif. Technol. 2015, 150, 229–242.

15. Lata, S.; Samadder, S.R. Removal of arsenic from water using nano adsorbents and challenges: A review. J. Environ. Manag. 2016, 166, 387–406.

16. Burakov, A.E.; Galunin, E.V.; Burakova, I.V.; Kucherova, A.E.; Agarwal, S.; Tkachev, A.G.; Gupta, V.K. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. Ecotoxicol. Environ. Saf. 2018, 148, 702–712.

17. Awual, M.R.; Rahman, I.M.M.; Yaita, T.; Khaleque, M.A.; Ferdows, M. pH dependent Cu(II) and Pd(II) ions detection and removal from aqueous media by an efficient mesoporous adsorbent. Chem. Eng. J. 2014, 236, 100–109.

18. Awual, M.R. A novel facial composite adsorbent for enhanced copper(II) detection and removal from wastewater. Chem. Eng. J. 2015, 266, 368–375.

19. Reddy, D.H.K.; Yun, Y.S. Spinel ferrite magnetic adsorbents: Alternative future materials for water purification? Coord. Chem. Rev. 2016, 315, 90–111.

20. Mo, J.H.; Yang, Q.; Zhang, N.; Zhang, W.X.; Zheng, Y.; Zhang, Z. A review on agro-industrial waste (AIW) derived adsorbents for water and wastewater treatment. J. Environ. Manag. 2018, 227, 395–405.

21. Doan, V.D.; Tran, T.K.N.; Nguyen, A.T.; Tran, V.A.; Nguyen, T.D.; Le, V.T. Comparative study on adsorption of cationic and anionic dyes by nanomagnetite supported on biochar derived from Eichhornia crassipes and Phragmites australis stems. Environ. Nanotechnol. Monit. Manag. 2021, 16, 100569.

22. Zhou, Y.B.; Lu, J.; Zhou, Y.; Liu, Y.D. Recent advances for dyes removal using novel adsorbents: A review. Environ. Pollut. 2019, 252, 352–365.

23. Tran, V.A.; Kadam, A.N.; Lee, S.W. Adsorption-assisted photocatalytic degradation of methyl orange dye by zeolite-imidazole-framework-derived nanoparticles. J. Alloy. Compd. 2020, 835, 155414.

24. O'Connor, S.J.; MacKenzie, K.J.D.; Smith, M.E.; Hanna, J.V. Ion exchange in the charge-balancing sites of aluminosilicate inorganic polymers. J. Mater. Chem. 2010, 20, 10234–10240.

25. Skorina, T. Ion exchange in amorphous alkali-activated aluminosilicates: Potassium based geopolymers. Appl. Clay Sci. 2014, 87, 205–211.

26. Duan, P.; Yan, C.; Zhou, W.; Ren, D. Development of fly ash and iron ore tailing based porous geopolymer for removal of Cu(II) from wastewater. Ceram. Int. 2016, 42, 13507–13518.

27. Kara, I.; Tunc, D.; Sayin, F.; Akar, S.T. Study on the performance of metakaolin based geopolymer for Mn(II) and Co(II) removal. Appl. Clay Sci. 2018, 161, 184–193.

28. Liu, Y.; Yan, C.J.; Zhang, Z.H.; Wang, H.Q.; Zhou, S.; Zhou, W. A comparative study on fly ash, geopolymer and faujasite block for Pb removal from aqueous solution. Fuel 2016, 185, 181–189.

29. Kara, İ.; Yilmazer, D.; Akar, S.T. Metakaolin based geopolymer as an effective adsorbent for adsorption of zinc(II) and nickel(II) ions from aqueous solutions. Appl. Clay Sci. 2017, 139, 54–63.

30. Lan, T.; Li, P.F.; Rehman, F.U.; Li, X.L.; Yang, W.; Guo, S.W. Efficient adsorption of Cd2+ from aqueous solution using metakaolin geopolymers. Environ. Sci. Pollut. Res. 2019, 26, 33555–33567.

31. Yan, C.J.; Guo, L.; Ren, D.M.; Duan, P. Novel composites based on geopolymer for removal of Pb(II). Mater. Lett. 2019, 239, 192–195.

32. Yan, S.; Zhang, F.Y.; Wang, L.; Rong, Y.D.; He, P.G.; Jia, D.C.; Yang, J.L. A green and low-cost hollow gangue microsphere/geopolymer adsorbent for the effective removal of heavy metals from wastewaters. J. Environ. Manag. 2019, 246, 174–183.

33. Abdelrahman, E.A.; Abou El-Reash, Y.G.; Youssef, H.M.; Kotp, Y.H.; Hegazey, R.M. Utilization of rice husk and waste aluminum cans for the synthesis of some nanosized zeolite, zeolite/zeolite, and geopolymer/zeolite products for the efficient removal of Co(II), Cu(II), and Zn(II) ions from aqueous media. J. Hazard. Mater. 2021, 401, 123813.

34. Luukkonen, T.; Věžníková, K.; Tolonen, E.-T.; Runtti, H.; Yliniemi, J.; Hu, T.; Kemppainen, K.; Lassi, U. Removal of ammonium from municipal wastewater with powdered and granulated metakaolin geopolymer. Environ. Technol. 2017, 39, 414–423.

35. Luukkonen, T.; Sarkkinen, M.; Kemppainen, K.; Rämö, J.; Lassi, U. Metakaolin geopolymer characterization and application for ammonium removal from model solutions and landfill leachate. Appl. Clay Sci. 2016, 119, 266–276.

36. Sanguanpak, S.; Wannagon, A.; Saengam, C.; Chiemchaisri, W.; Chiemchaisri, C. Porous metakaolin-based geopolymer granules for removal of ammonium in aqueous solution and anaerobically pretreated piggery wastewater. J. Clean. Prod. 2021, 297, 126643.

37. Siyal, A.A.; Shamsuddin, M.R.; Rabat, N.E.; Zulfiqar, M.; Man, Z.; Low, A. Fly ash based geopolymer for the adsorption of anionic surfactant from aqueous solution. J. Clean. Prod. 2019, 229, 232–243.

38. Runtti, H.; Luukkonen, T.; Niskanen, M.; Tuomikoski, S.; Kangas, T.; Tynjälä, P.; Tolonena, E.T.; Sarkkinen, M.; Kemppainen, K.; Rämö, J.; et al. Sulphate removal over barium-modified blast-furnace-slag geopolymer. J. Hazard. Mater. 2016, 317, 373–384.

39. Cheng, T.W.; Lee, M.L.; Ko, M.S.; Ueng, T.H.; Yang, S.F. The heavy metal adsorption characteristics on metakaolin-based geopolymer. Appl. Clay Sci. 2012, 56, 90–96.

40. Novais, R.M.; Carvalheiras, J.; Tobaldi, D.M.; Seabra, M.P.; Pullar, R.C.; Labrincha, J.A. Synthesis of porous biomass fly ash-based geopolymer spheres for efficient removal of methylene blue from wastewaters. J. Clean. Prod. 2019, 207, 350–362.

41. Papa, E.; Mor, M.; Natali Murri, A.; Landi, E.; Medri, V. Ice-templated geopolymer beads for dye removal. J. Colloid Interface Sci. 2020, 572, 364–373.

42. Maleki, A.; Mohammad, M.; Emdadi, Z.; Asim, N.; Azizi, M.; Safaei, J. Adsorbent materials based on a geopolymer paste for dye removal from aqueous solutions. Arab. J. Chem. 2020, 13, 3017–3025.

43. Yan, S.; He, P.G.; Jia, D.C.; Wang, Q.G.; Liu, J.J.; Yang, J.L.; Huang, Y. Synthesis of novel low-cost porous gangue microsphere/geopolymer composites and their adsorption properties for dyes. Int. J. Appl. Geram. Technol. 2018, 15, 1602–1614.

44. Li, L.; Wang, S.; Zhu, Z. Geopolymeric adsorbents from fly ash for dye removal from aqueous solution. J. Colloid Interface Sci. 2006, 300, 52–59.

45. Hua, P.; Sellaoui, L.; Franco, D.; Netto, M.S.; Luiz Dotto, G.; Bajahzar, A.; Belmabrouk, H.; Bonilla-Petriciolet, A.; Li, Z. Adsorption of acid green and procion red on a magnetic geopolymer based adsorbent: Experiments, characterization and theoretical treatment. Chem. Eng. J. 2020, 383, 123113.

46. Açışlı, Ö.; Acar, İ.; Khataee, A. Preparation of a surface modified fly ash-based geopolymer for removal of an anionic dye: Parameters and adsorption mechanism. Chemosphere 2022, 295, 133870.

47. Barbosa, T.R.; Foletto, E.L.; Dotto, G.L.; Jahn, S.L. Preparation of mesoporous geopolymer using metakaolin and rice husk ash as synthesis precursors and its use as potential adsorbent to remove organic dye from aqueous solutions. Ceram. Int. 2018, 44, 416–423.

48. Pinto, L.F.; Montao, A.M.; González, C.; Barón, G. Removal of rhodamine B in wastewater from the textile industry using geopolymeric material. J. Phys. Conf. Ser. 2019, 1386, 012040.

49. Fumba, G.; Essomba, J.S.; Tagne, G.M.; Nsami, J.N.; Mbadcam, J.K. Equilibrium and kinetic adsorption studies of methyl orange from aqueous solutions using kaolinite, metakaolinite and activated geopolymer as low cost adsorbents. J. Acad. Ind. Res. 2014, 3, 156–163.

50. Oliveira, K.G.; Botti, R.; Kavun, V.; Gafiullina, A.; Franchin, G.; Repo, E.; Colombo, P. Geopolymer beads and 3D printed lattices containing activated carbon and hydrotalcite for anionic dye removal. Catal. Today 2022, 390–391, 57–68.

51. Siyal, A.A.; Shamsuddin, M.R.; Khan, M.I.; Rabat, N.E.; Zulfiqar, M.; Man, Z.; Siame, J.; Azizli, K.A. A review on geopolymers as emerging materials for the adsorption of heavy metals and dyes. J. Environ. Manag. 2018, 224, 327–339.

52. Boscherini, M.; Miccio, F.; Papa, E.; Medri, V.; Landi, E.; Doghieri, F.; Minelli, M. The relevance of thermal effects during CO2 adsorption and regeneration in a geopolymer-zeolite composite: Experimental and modelling insights. Chem. Eng. J. 2021, 408, 127315.

53. Minelli, M.; Medri, V.; Papa, E.; Miccio, F.; Landi, E.; Doghieri, F. Geopolymers as solid adsorbent for CO2 capture. Chem. Eng. Sci. 2016, 148, 267–274.

54. Minelli, M.; Papa, E.; Medri, V.; Miccio, F.; Benito, P.; Doghieri, F.; Landi, E. Characterization of novel geopolymer—Zeolite composites as solid adsorbents for CO2 capture. Chem. Eng. J. 2018, 341, 505–515.

55. Candamano, S.; Policicchio, A.; Macario, A.; Conte, G.; Agostino, R.G.; Frontera, P.; Crea, F. CO2 Adsorption Investigation on an Innovative Nanocomposite Material with Hierarchical Porosity. J. Nanosci. Nanotechnol. 2019, 19, 3223–3231.

56. Papa, E.; Medri, V.; Paillard, C.; Contri, B.; Natali Murri, A.; Vaccari, A.; Landi, E. Geopolymer-hydrotalcite composites for CO2 capture. J. Clean. Prod. 2019, 237, 117738.

57. Novikova, L.A.; Bogdanov, D.S.; Belchinskaya, L.I.; Kolousek, D.; Doushova, B.; Lhotka, M.; Petukhova, G.A. Adsorption of formaldehyde from aqueous solutions using metakaolin-based geopolymer sorbents. Prot. Met. Phys. Chem. Surf. 2019, 55, 864–871.

58. Saha, B.; Vedachalam, S.; Dalai, A.K. Performance of geopolymer as adsorbent on desulphurization of heavy gas oil. Can. J. Chem. Eng. 2021, 99, 2355–2367.

59. Della Rocca, D.G.; Peralta, R.M.; Peralta, R.A.; Rodríguez-Castellón, E.; Moreira, R.D.P.M. Adding value to aluminosilicate solid wastes to produce adsorbents, catalysts and filtration membranes for water and wastewater treatment. J. Mater. Sci. 2020, 56, 1039–1063.

60. Novais, R.M.; Ascensão, G.; Tobaldi, D.M.; Seabra, M.P.; Labrincha, J.A. Biomass fly ash geopolymer monoliths for effective methylene blue removal from wastewaters. J. Clean. Prod. 2018, 171, 783–794.

61. Ge, Y.Y.; Yuan, Y.; Wang, K.T.; He, Y.; Cui, X.M. Preparation of geopolymer-based inorganic membrane for removing Ni2+ from wastewater. J. Hazard. Mater. 2015, 299, 711–718.

62. Wang, J.T.; Ge, Y.Y.; He, Y.; Xu, M.X.; Cui, X.M. A porous gradient geopolymer-based tube membrane with high PM removal rate for air pollution. J. Clean. Prod. 2019, 217, 335–343.

63. De Sousa, F.A.; Della-Rocca, D.; de Amorim, S.M.; Salla, J.D.; Peralta, R.A.; Rodríguez-Castellón, E.; Moreira, R.F.P.M. Development of Membranes Based on Alkali-Activated Phosphate Mine Tailings for Humic Acid and Copper Removal from Water. Water Air Soil Pollut. 2021, 232, 496.

64. Xu, M.X.; He, Y.; Liu, Z.H.; Tong, Z.F.; Cui, X.M. Preparation of geopolymer inorganic membrane and purification of pulp-papermaking green liquor. Appl. Clay Sci. 2019, 168, 269–275.

65. Zhang, J.B.; Ge, Y.Y.; Li, Z.L.; Wang, Y.P. Facile fabrication of a low-cost and environmentally friendly inorganic-organic composite membrane for aquatic dye removal. J. Environ. Manag. 2020, 256, 109969.

66. Zhang, J.B.; Ding, S.Y.; Ge, Y.Y.; Li, Z.L. Enhanced removal of crystal violet in water using a facile-fabricated and environmental-friendly laccase immobilized composite membrane. Process Biochem. 2020, 98, 122–130.