Synthesis of geopolymer for the removal of hazardous waste: a review

Rasha A. Al-husseiny* and Shahlaa E. Ebrahim
1Environmental Engineering Department, University of Baghdad

E-mail: rashaali.taha1983@gmail.com

Abstract. Water is the most essential material on Earth; any pollution of water can have adverse effects on living beings. Today, the elimination of harmful pollutants from water is one of the most critical concerns; in this respect, the application of a minimum quantity of chemicals or the use of natural substances for pollutant elimination is of serious importance. This review discusses the study work that is carried out on adsorbent synthesis from different natural substances, such as (kaolinite, metakaolin, fly ash, etc). This adsorbent is known as geopolymer. An attention to the geopolymer was paid to its specific three-dimensional network structure, with defined pore sizes. The review shall include the elemental and sorts of materials used in the creation of adsorbents and the impact of parameters like as (pH, contact time, adsorbent dose, temperature and initial concentration) on the adsorption capacity of hazardous waste. In addition to enhance the adsorption characteristics of natural substances and producing high-quality adsorbents, different synthesis techniques have been produced. One of the most successful methods is to precipitate nanoparticles on the geopolymer surface. This development would improve the adsorbent surface area, mechanical strength and resistance to chemical compounds, by means of that improving its ability for adsorption of contaminants.

Keywords: Natural adsorbent, geopolymer, adsorption capacity, kaoline, fly ash, slag

1. Introduction

A great variety of contaminants such as heavy metals, [1], dyes, pharmaceuticals [2][3], pesticides, surfactants and home healthcare items have polluted water supplies. These contaminants are environmentally harmful to humans and animals [4]. Various wastewater treatment techniques like flocculation, membrane processes, adsorption, absorption, ion exchange, electrolytic isolation, reduction, and reverse osmosis techniques. However, these systems have a variety of drawbacks, i.e., expensive facilities, higher maintenance and high operating costs. [5]. Adsorption is considered to be the most effective method for removing contaminants in wastewater, because it is simple and cost-effective method [6]. The adsorbent matter can be mineral, organic or biological. Activated carbon is the preferred, conventional material at the industrial scale [7]. Recently, most of the materials used as adsorbent, like fly ash [8], metakaolin [9], kaolin and slag [10] Can be used as one of the developing materials as an adsorbent based geopolymer [11]. Davidovits was the first person who coined the term geopolymer in 1978 to characterize a wide materials range, which characterized by inorganic molecules’ networks or chains. Geopolymers a promising category of materials is intended to remove toxic substances from industrial and household waste. Over the last decade, alkali-activation (or geopolymer) technology has gained a lot of interest in its possible applications in the treatment of water and waste water. [12]. The characteristics of geopolymers depend mainly on the properties of the precursor materials (chemical composition, glass phase, the quantity of soluble silicon and aluminum, morphology of particles, mineralogical structure, distribution of particle size, and existence of inert particles). The excellent foundation materials should have sufficient spherical glass bead content and have an extremely amorphous structure. [13]. For the reason that many adsorbents are inexpensive and have lower resistance to environmental variations like as pH. In this sense, improvement of the surface by chemically resistant materials of cost effective natural adsorbents like geopolymers is considered to be a key factor in overcoming these challenges [14]. The aim of this
review, is to present the production of a low-cost adsorptive media for the removal of hazardous waste and the precursor for the synthesis of this media from waste or raw material with high capacity, uniform properties and ease of preparation such as geopolymer. This review shows effect of modification on the geopolymer and other natural materials on the adsorption capacity by precipitating or coating of nanomaterial on their surface.

2. Geopolymer structure

The suggested terminology of the geopolymer structure categorizes geopolymers into three elementary forms based on their Si/Al ratios, which are poly (sialate-disiloxo), poly (sialate-siloxo) and poly (sialate), as seen in the Figure 1[15].

![Figure 1: Various systems of geopolymer depending on the siloxo number of Si-O units [15]](image)

3. Synthesis of geopolymer

There are two synthesize routes used in the synthesis of geopolymer [16].

1- Alkali route: the geopolymer is synthesized in this route using alkali medium containing one or two or more hydroxide solutions (Na+, Ca+7+, K+, Cs+).

2- Acidic route: in which phosphoric acid (H₃PO₄) is used for the development of polyaluminum phosphate geopolymer as a medium

The most suggested mechanism for geopolymer synthesis shall include the following four stages:[17]

1) Dissolution of Si and Al from solid alumino silicate materials in extremely alkaline aqueous solution as shown in equation (1)

\[ (SiO_2, Al_2O_3) + 2MOH + 5H_2O \rightarrow Si(OH)_4 + 2Al(OH)_4^- + 2M \]  \(\text{(1)}\)

Where: M symbolize Na or K.

2) Creation of Si and / or Si-Al oligomers in the aqueous phase. Equations (2), (3) and (4)

\[ Si(OH)_4 + Si(OH)_4 \leftrightarrow (OH)_3Si - O - Si(OH)_3 + H_2O \]  \(\text{(2)}\)

\[ Si(OH)_4 + Al(OH)_4 \leftrightarrow (OH)_3Si - O - Al(=)(OH) + H_2O \]  \(\text{(3)}\)

\[ 2Si(OH)_4 + Al(OH)_4 \leftrightarrow (OH)_3Si - O - Al(=)(OH) + 2H_2O \]  \(\text{(4)}\)

3) Polycondensation of the oligomers to form a three-dimensional aluminosilicate framework. as it is presented by chemical Equations (5a) and (5b):
n[(OH)\(_3\)Si-O-Si(OH)\(_3\)] \rightarrow (-Si-O-Si-O\(^-\))\(_n\)+3nH\(_2\)O \quad \text{(5a)}

n[(OH)\(_3\)Si-O-Al\(^{3+}\)(OH)\(_3\)] \rightarrow (-Si-O-Al\(^{3+}\)O\(^-\))\(_n\)+3nH\(_2\)O \quad \text{(5b)}

4) Linking of the solid particles into the geopolymeric structure and hardening into a final solid polymeric structure of the overall system. Within the Chemical Equation (6).

\[> T - OH + HO(- Si-O-Al-O\(_n\)) > T-O(- Si-O-Al-O\(_n\)) + H\(_2\)O \quad \text{(6)}\]

Where: (> T) indicate to Si surface or Al sites

Geopolymers are inorganic polymeric materials produced by the alkali activation of aluminosilicate materials in metakaolin, fly ash and granulated blast furnace slag (GBFS). Widely used alkali activators contain sodium and potassium hydroxide with sodium and potassium silicate is also applied to geopolymer preparation [11]. The formulation of geopolymers involves different stages: the release of silicate and aluminate, gelation, polymerization and hardening. There is various material used as precursor for synthesis geopolymer as shown below:

### 3.1 Kaolinite

Kaolinite (Kaol) is primarily a layered white clay mineral denoted as shown in figure (2) by the chemical composition Al\(_2\)Si\(_2\)O\(_5\)(OH)\(_4\) [18]. Impurities or significant amounts of other minerals such as montmorillonite or iron oxides are commonly found in colored forms of kaolinite clay. Kaolinite formation occurs by hydrothermal alteration or the breaking down of acid igneous rocks containing silicate aluminum, such as feldspars and muscovites. As well as it can be used in granite and gneiss. Kaolinite-rich rock is usually referred to as kaolinite [19].

![Figure 2: Kaolinite structure](image)

Kaolin is a phyllosilicate, composed of alternating layers of silica and aluminum in octahedral and tetrahedral coordination. This electrically neutral crystalline layer formation, which is a typical feature of clay minerals, contributes to a fine particle size and a plate-like morphology, allowing the particles to pass through. Easily across each other, Giving rise to physical properties such as softness, soapy feeling and basic cleavage[20].

### 3.2 Metakaolinite

Metakaolin rather than kaolinite as a source material provides specific advantages in terms of high reactivity and purity. [21]. Metakaolin is an anhydrous aluminosilicate clay mineral with the chemical composition Al\(_2\)Si\(_2\)O\(_5\)(OH)\(_4\) formed by tetrahedral silica layer and one octahedral alumina layer. This
also results in a geopolymer with higher compressive strength, high surface area and large porous surfaces[22]. The properties i.e. purity, crystalline high surface areas, and metal oxides) make geopolymers based on metakaolin a very interesting group.[23][24].Table (1) illustrated the chemical composition of metakaolin based geopolymer adsorbent.

| Table 1: Chemical composition of metakaolin based geopolymer adsorbent[25] |
|-----------------|----------------|-------------|---------|---------|---------|---------|---------|
| Oxide          | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO     | K₂O     | MgO     | TiO₂    |
| Weight percent W, % | 52   | 42.8  | 0.6   | 0.2     | 0.5     | -       | 1.2     |
|                 |      |       |       |         |         |         | 0.6     |

3.3 Fly ash
Fly ash is one of the residues produced during the combustion of coal in the coal power plant [26]. Fly ash performance in geopolymers is highly affected by its physical, chemical and mineralogical properties. The mineralogical and chemical composition as shown in Table 1 depends mainly on coal composition [27]. Fly ash can be classified into two groups depending on its source and constitution. Class F of the fly ash is generated from the burning of bituminous or anthracite coal and follows this chemical composition \((\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \geq 70\%\) as shown in Table 2. Class C is usually formed from the combustion of sub-bituminous or lignite coal and has the following chemical composition. \((\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \geq 50\%\) [28]. [29] prepare geopolymer successfully from calcined fly ash and using it for adsorption of various pollutant.

| Table 2: chemical composition of fly ash class F [27] |
|-----------------|-------------|-------------|---------|---------|---------|---------|
| Oxide | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | K₂O | MgO | TiO₂ | Na₂O | P₂O₅ |
| Weight percent W, % | 48 | 29 | 10 | 6.5 | 2.5 | 2 | 1.3 | 0.6 | 0.4 |

3.4 Slag
Blast furnace slag (BFS) is a non-metallic residual material used in the manufacture of steel. Blast furnaces are fed with controlled mixtures of iron ore \((\text{Fe}_2\text{O}_3 + \text{SiO}_2)\), coke \((\text{C})\), and limestone \((\text{CaCO}_3)\), and work at temperatures about 2000°C. The resulting material is steel and residual slag [30]. [31] used a blast furnace slag (BFS) with a fly ash (FA) based geopolymer adsorbent to remove \(\text{Pb}^{2+}\) from aqueous solutions which were synthesized using the hydrothermal process at 60 C for 24 h, and then cured at 25 C for a further six days. [10] use the metakaoline with slag as the base of the geopolymer with the chemical composition of the slag. as shown in table (3):

| Table 3: Chemical compositions of slag |
|-----------------|-------------|-------------|---------|---------|---------|---------|
| Oxide | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | K₂O | MgO | TiO₂ | SO₃ | LOI |
| Weight percent W, % | 34.2 | 14.2 | 0.43 | 41.7 | - | 6.7 | 1.07 | 1.47 | 1.02 |

3.5 Rice husk ash
Because of the raised generation of biomass ash as a waste of thermal biomass. alternative reuse mechanisms for ash helps to verify the economic viability of biomass-based energy [32]. Rice husk ash is one of the wastes of biomass used as the precursor for geopolymer synthesis with other raw material such as metakaolin [33] and fly ash. [32] determined the effect of the biomass ash combine on
the main engineering characteristics of the geopolymer and the conformity of these characteristics with industrial standards.

4. Adsorption experiments on the geopolymer

Recent times, geopolymers have been commonly used for wastewater treatment due to porous composition and relatively inexpensive. Geopolymers have also been successfully used for the adsorption of heavy metals such as Cd, Ni, Pb ions, boron, fluoride, phosphate, radionuclide $^{137}$Cs and $^{90}$Sr, $Cu^{2+}$, and $Ni^{2+}$[34][35] and dyes like methylene blue (MB)[36]. Table (4) illustrated the effect of using geopolymer from different precursor for treatment of different types of adsorbate on adsorption capacity.

5. Modification on the natural material

Recently, several researchers have been concentrating their attention to enhance adsorption properties of natural materials and developing high-quality adsorbents. A variety of synthesis techniques have been developed to address this issue. One of the most successful methods was to coat the adsorbent surface with nanoparticles. This development would improve the adsorbent surface area, mechanical strength and resistance to chemical compounds. Thus, its potential for adsorption contaminants[37][38]. In recent years, one of the nano size particles synthesis and utilized in adsorption process is iron oxide $Fe_3O_4$ because of its scale in nano-range, high surface-to-volume ratios and super para magnetism [39]. However, the use of pure $Fe_3O_4$ nanoparticles as adsorbent media are not desirable for economic purposes. Moreover, nanoparticles tend to agglomerate, resulting in a major loss of reactivity [40]. To overcome this challenge and improve the quality of treatment and the ability of natural material to eliminate pollutants, a developed method of precipitating or coating nano-sized particles onto the surface of the natural material has been adopted. Like the Geopolymer, zeolite [38], bentonite [41]. Table 5 present the effect of modification on the natural material on the performance of adsorption capacity.

6. Conclusion

This paper identified various forms of geopolymers for the adsorption of hazardous waste, like dyes and heavy metals, and illustrated the geopolymer synthesis mechanism. High performance, mechanical durability, environmentally friendly and cost-effectiveness has drawn a great deal of attention to geopolymers as the adsorption materials for these contaminants. Its application needs to be applied to other water and wastewater contaminants such as medicines, oil and grease (O&G), phenols, micropollutants, and others. Geopolymer efficiency requires additional improvement of adsorption capacity and rate of adsorption; for future work, geopolymers should be modified by precipitating nanomaterial on their surface to increase adsorption capacity. This could render the geopolymers the next innovative material of the future.
| precursor of geopolymer | Adsorbate type | Initial concentrati on | Adsorben t dose g/L | pH range | Conta ct time | Temperatu re °C | Stirrin g rate RPM | Adsorptio n capacity mg/g | Referenc es |
|------------------------|----------------|-----------------------|---------------------|----------|--------------|-----------------|-------------------|------------------------|------------|
| MKG                   | Cu(II) and Cr(VI) | -                     | (0-10)              | (2-7)    | Optimum 5    | 30              | 180               | 108.2 and 95.3       | [42]       |
| Rice husk RH, Rice husk ash RHA, palm oil fuel ash POFA, and ground granulated blast furnace slag GBGS | dye methylene blue | 100 ml of 10^-3 M | 0.1 | (3-8) | Optimum 3 | 1440 min | Room temperature | - | - | [43] |
| Clay and RH GP-1 and GP-2 and GP-3 | dye methylene blue | 25mg/L | 4 | (4-12) | Optimum 10 | 20 -80 min | 25°C ± 1 | 120 | 15.95, 17.89 and 20.22 | [44] |
| “Meta kaolin based geopolymer” MKG | Zn (II) and Ni(II) | 25-600 | 0.4-4 | (2-8)= 6.39 | 40 min | 25 °C | - | 74.53 | 42.61 | [45] |
| MKG & blast-furnace slag | Ni(II), As(III) Sh(III) | - | - | 4-8 | 180 min | - | - | 3.74 | 0.52 | 0.34 | [46] |
| Fly ash F (FAF-GP) blast furnace slag (BFS-GP) fibre sludge (FSSH-Ca-GP) | phosphate | 100 | 2 | 2 | 4 | (9-12) | 1.5hr | Room temperature | - | 26 | 36 | 43 | [47] |
| FA with geopolymeric monoliths | Lead | 50 | - | 5 for wfA and 7 for n-wfA | 3 and 24 hours | Room temperature | - | 0.95 -6.34 | [48] |
| MKG | dye methylene blue | (5-60 mg/L) Optimum 40mg/L | 0.05–0.35 g 0.1g/100 ml | (2-13) | (0–220) | 120 min | (20–70°C) | (250 rpm) | 43.48 | [49] |
| Litz Donawitz converter slag LD Slag | Ni(II) | (75-175) | 0.2g/100 ml | 4-10 | Optimum 9 | 24 hr | room temperature | - | 85.29 | mg/g | [50] |
| LD Slag | Zn (II) | (50-150) | 0.25 g/L | 4-9 | 0-200 min | - | - | 86 mg/g | [51] |
| Kaolinite | Pb (II), Cd (II) and Zn (II) | (10-100) ppm | 0.2 g/20 ml | (4, 5 and 6) | 30 min-24 hr | (25, 35 and 45°C) | - | 22 mg/g | [52] |
| MK | Pb^{2+}, Cu^{2+}, Cr^{3+}, and Cd^{2+} | 100 ppm | 0.0200.000 1 | 2-5 | 24 hr | 15-45 | - | Pb^{2+}=86, 2 mg/g, Cr^{3+}=9.79 mg/g, Cu_{2}=40, 9 mg/g, Cd^{2+}=68.8 | [21] |
| Fly ash | methylene blue and crystal violet | 10-6–10-5 M | 0.02 g/100 ml | 6.3 | 24 hr | 30 and 40 °C | 100 rpm | 1.2 × 10-4 and 2.4 × 10-4 mol/g | [53] |
| Metakaolin | Formnaldehyde de Na^+Cu^{2+}, Na H^+ | 0.13 to 0.2 mol/L | - | - | 0.5,1.2 ,4 | 20°C | 30 min | 0.81,1.69 ,1.69 mmol/g | [54] |
### Table 5: Effect of modification on the natural material on the adsorption capacity

| Natural material                        | Adsorbate                  | pH | Adsorption capacity (mg g⁻¹) | References |
|-----------------------------------------|----------------------------|----|------------------------------|------------|
| Fe₃O₄/Bentonite                         | Cobalt(II)                 | 9  | 18.76                       | [55]       |
| chitosan-bound Fe₃O₄                   | Cu(II)                     | ≥ 2| 21.5                        | [56]       |
| MnFeO₄/bentonite                        | acid red 138               | 2  | 23.5                        | [57]       |
| MnFeO₄/kaolin                          | Acid Red 151               | 2  | 576                         | [58]       |
| Chitosan coated perlite beads          | Co (II) metal ions         | 5  | 135.1                       | [59]       |
| Clay–iron oxide magnetic               | Ni²⁺, Cu²⁺, Cd²⁺, and Zn²⁺ | 5  | 40, 50, 74, and 75          | [60]       |
| kaolinite-supported zero-valent iron nanoparticles | Cu²⁺ and Co²⁺ ions | 7  | 25 and 140                  | [61]       |
| Iron oxide/Bentonite                   | nickel                     | 5.5| 21                          | [62]       |
| CuFeO₄/activated carbon                | acid orange II             | 5.2| 392                         | [63]       |
| magnetic coated zeolite                | pharmaceutical             |    | 97                          | [39]       |
| bentonite (NB) coated with synthesized Fe₃O₄ magnetite | Cu(II) ions                | 6  | 46.948                      | [41]       |
| clay aggregate surface by coating with MgO nanoparticles | Metronidazole antibiotic | 5 and 9 | 56.31 to 84.55 mg/g        | [64]       |
| geopolymer and amorphous hydrous ferric oxide | arsenic                      | 5.38| 560 µg As/g                 | [65]       |
| activated carbon and bentonite         | amoxicillin                | 7.01| 47.37                       | [66]       |
| Mt-Kaolinite/TiO₂                       | Pb                         | 2-6.4| 71.1                        | [67]       |

### References

[1] Alkurdy F A R and Ebrahim S E 2020 Comparison Between Commercial and Synthesized Fe₃O₄ Nanoparticles for Removal of Heavy Metal Contaminants in Wastewater,” Assoc. Arab Univ. J. Eng. Sci., doi: 10.33261/jaaru.2019.27.1.004.

[2] Yuan X, Qiang Z, Ben W, Zhu B and Liu J 2014 Rapid detection of multiple class pharmaceuticals in both municipal wastewater and sludge with ultra high performance liquid chromatography tandem mass spectrometry, J. Environ. Sci. (China), 26(9):1949–59, doi: 10.1016/j.jes.2014.06.022.

[3] Al Qarni H, Collier P, O’Keeffe J and Akunna J 2016 Investigating the removal of some pharmaceutical compounds in hospital wastewater treatment plants operating in Saudi Arabia, Environ. Sci. Pollut. Res., doi: 10.1007/s11356-016-6389-7.

[4] Da’na E 2017 Adsorption of heavy metals on functionalized-mesoporous silica: A review, Microporous and Mesoporous Materials., doi: 10.1016/j.micromeso.2017.03.050.

[5] Sharma Y C, Srivastava V, Singh V K, Kaul S N and Weng C H 2009 Nano-adsorbents for the removal of metallic pollutants from water and wastewater, Environmental Technology., doi: 10.1080/09593330902838080.

[6] Adriano W S, Veredas V, Santana C C and Gonçalves L R B 2005 Adsorption of amoxicillin on chitosan beads: Kinetics, equilibrium and validation of finite bath models, Biochem. Eng. J., 27(2):132–7.

[7] Crini G, Lichtfouse E, Wilson L D and Morin-Crini N 2019 Conventional and non-conventional adsorbents for wastewater treatment,” Environ. Chem. Lett., 17(1):195–213.
[8] Novais R M, Ascensão G, Tobaldi D M, Seabra M P and Labrincha J A, 2018 Biomass fly ash geopolymer monoliths for effective methylene blue removal from wastewaters, J. Clean. Prod., 171, pp.783–94.

[9] Selmani S, Sdiri A, Bouazziz S, Joussein E and Rossignol S 2017 Effects of metakaolin addition on geopolymer prepared from natural kaolinitic clay,” Appl. Clay Sci., 146(June):457–67.

[10] Yunsheng Z, Wei S Qianli C and Lin C 2007 Synthesis and heavy metal immobilization behaviors of slag based geopolymer, J. Hazard. Mater., doi: 10.1016/j.jhazmat.2006.09.033.

[11] N. Ariffin, M. M. A. B. Abdullah, R. R. M. A. Zainol, and M. F. Murshed, “Geopolymer as an adsorbent of heavy metal: A review,” in AIP Conference Proceedings, 2017, doi: 10.1063/1.5002224.

[12] Luukkonen T, Heponiemi A, Runtti H, Pesonen J, Yliniemi J and Lassi U 2019 Application of alkali-activated materials for water and wastewater treatment: a review, Rev. Environ. Sci. Biotechnol., 18(2):271–97.

[13] Sumesh M, Alengaram U J, Jumaat M Z, Mo K H and Alnahhal M F 2017 Incorporation of nano-materials in cement composite and geopolymer based paste and mortar – A review,” Construction and Building Materials., doi: 10.1016/j.conbuildmat.2017.04.206.

[14] Saravanan R, Gupta V K, Narayanan V and Stephen A 2014 Visible light degradation of textile effluent using novel catalyst ZnO/γ-Mn2O3, ” J. Taiwan Inst. Chem. Eng., 45(4):1910–7.

[15] Davidovits P J 2002 30 Years of Successes and Failures in Geopolymer Applications . Market Trends and Potential Breakthroughs , Geopolymer 2002 Conf.

[16] Davidovits J, 2017 Geopolymers: Ceramic-like inorganic polymers, J. Ceram. Sci. Technol, 8(3):335–50.

[17] Panias D, Giannopoulou I P and Perraki T 2007 Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers,” Colloids Surfaces A Physicochem. Eng. Asp., 301(1–3):246–54.

[18] P. Leinster, R. Perry, and R. J. Young, “Ethylene dibromide in urban air,” Atmos. Environ., 1978, doi: 10.1016/0004-6981(78)90280-9.

[19] Mukherjee S and Ghosh B 2013 The science of clays: Applications in industry, engineering and environment..

[20] Rashad A M 2013 Alkali-activated metakaolin: A short guide for civil Engineer-An overview,” Construction and Building Materials. doi: 10.1016/j.conbuildmat.2012.12.030.

[21] Cheng T W, Lee M L, Ko M S, Ueng T H and Yang S F 2012 The heavy metal adsorption characteristics on metakaolin-based geopolymer, Appl. Clay Sci., doi: 10.1016/j.clay.2011.11.027.

[22] Strini A et al., 2016 TiO2-based photocatalytic geopolymers for nitric oxide degradation, Materials (Basel)., doi: 10.3390/ma9070513.

[23] Tang Q, He Y, pin Wang Y, tuo Wang K and min Cui X 2016 Study on synthesis and characterization of ZSM-20 zeolites from metakaolin-based geopolymers, Appl. Clay Sci, doi: 10.1016/j.clay.2016.05.011.

[24] Trivunac K, Kljajević L M and Nenadović S 2016 Microstructural characterization and adsorption properties of alkali-activated materials based on metakaolin, Sci. Sinter., doi: 10.2298/SOS1602209T.

[25] López F J, Sugita S, Tagaya M, and Kobayashi T 2014 Metakaolin-based geopolymers for targeted adsorbents to heavy metal ion separation, J. Mater. Sci. Chem. Eng., 2(07):16.

[26] Zainal F F, Fazill M F, Hussin K, Rahmat A, Abdullah M M A B and Wazien W 2018 Effect of geopolymer coating on mild steel, ” Solid State Phenom., 273SSP (July):175–80.

[27] Burduhos Nergis D D, Vizureanu P and Corbu O 2019 Synthesis and characteristics of local fly ash based geopolymers mixed with natural aggregates,” Rev. Chim., 70(4):1262–7.

[28] Thomas M D A 2007 Optimizing the use of fly ash in concrete, 5420. Portland Cement Association Skokie, IL.
[29] Tian Q and Sasaki K, 2019 Structural characterizations of fly ash-based geopolymer after adsorption of various metal ions,” Environ. Technol. (United Kingdom), 0(0):1–11.
[30] Siddique R and Khan M I, 2011 Ground granulated blast furnace slag, in Supplementary cementing materials, Springer, pp.121–73.
[31] de Matos P R et al. 2020 Use of air-cooled blast furnace slag as supplementary cementitious material for self-compacting concrete production,” Constr. Build. Mater., 262, p. 120102.
[32] Samadhi T W, Wulandari W, Prasetyo M I and Fernando M R 2017 Reuse of Coconut Shell, Rice Husk, and Coal Ash Blends in Geopolymer Synthesis,” IOP Conf. Ser. Mater. Sci. Eng., 248(1).
[33] Barbosa T R, Folleto E L, Dotto G L and Jahn S L 2018 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., 44(1):416–23.
[34] Al-Harahsheh M S, Al Zboon K, Al-Makhadmeh L, Hararah M and Mahasneh M. 2015 Fly ash based geopolymer for heavy metal removal: A case study on copper removal,” J. Environ. Chem. Eng., 3(3):1669–77.
[35] Ge Y, Yuan Y, Wang K, He Y and Cui X 2015 Preparation of geopolymer-based inorganic membrane for removing Ni2+ from wastewater, J. Hazard. Mater., 299, pp. 711–8.
[36] Alouani M E L, Alehyen S, Achouri M E L and Taibi M 2018 Removal of cationic dye—methylene blue—from aqueous solution by adsorption on fly ash—based geopolymer,” J. Mater. Environ. Sci., 9(1):32–46, 2018.
[37] Samarghandi M R, Al-Musawi T J, Mohseni-Bandpi A and Zarrabi M 2015 Adsorption of cephalixin from aqueous solution using natural zeolite and zeolite coated with manganese oxide nanoparticles, J. Mol. Liq., 211, pp. 431–441, 2015.
[38] Mohseni-Bandpi A, Al-Musawi T J, Ghahramani E, Zarrabi M, Mohebi S and Vahed S A 2016 Improvement of zeolite adsorption capacity for cephalixin by coating with magnetic Fe3O4 nanoparticles, J. Mol. Liq., 218, pp. 615–24, 2016.
[39] Salem Attia T M, Hu X L and Yin D Q 2013 Synthesized magnetic nanoparticles coated zeolite for the adsorption of pharmaceutical compounds from aqueous solution using batch and column studies,” Chemosphere, 93(9):2076–2085.
[40] Chen D, Li L and Guo L 2011 An environment-friendly preparation of reduced graphene oxide nanosheets via amino acid, Nanotechnology, 22(32):325601.
[41] Mohammed A A and Samaka I S 2018 Bentonite coated with magnetite Fe3O4 nanoparticles as a novel adsorbent for copper (II) ions removal from water/wastewater,” Environ. Technol. Innov., 10:162–74.
[42] Yu Z, Song W, Li J, and Li Q 2020 Improved simultaneous adsorption of Cu(II) and Cr(VI) of organic modified metakaolin-based geopolymer, Arab. J. Chem., 13(3):4811–23.
[43] Maleki A, Mohammad M, Emdadi Z, Asin N, Azizi M and Safaei J 2020 Adsorbent materials based on a geopolymer paste for dye removal from aqueous solutions, Arab. J. Chem., 13, no. (1):3017–25.
[44] Mbuvi H M, Maingi F M, Mbuvi H M, Ng’ang’ M M and Mwangi H 2017 Adsorption Kinetics and Isotherms of Methylene blue by Geopolymers Derived from Common Clay and Rice Husk Ash Exploring cheap adsorbent materials for water treatment View project Applying basic science for sustainable agriculture View project Adsorption K, Phys. Chem., 7(4):pp. 87–97.
[45] Kara I, Yilmazer D and Akar S T 2017 Metakaolin based geopolymer as an effective adsorbent for adsorption of zinc(II) and nickel(II) ions from aqueous solutions, Appl. Clay Sci., 139, pp. 54–63.
[46] Luukkonen T et al. 2016 Simultaneous removal of Ni(II), As(III), and Sh(III) from spiked mine effluent with metakaolin and blast-furnace-slag geopolymers, J. Environ. Manage., 166, pp 579–588.
[47] Samarina T and Takaluoma E 2019 New geopolymer adsorbents for phosphate removal from
diluted solutions and their applications, *Proc. World Congr. New Technol.*, **0**: pp. 2–3.

[48] Novais R M, Buruberri L H, Seabra M P and Labrincha J A 2016 Novel porous fly-ash containing geopolymer monoliths for lead adsorption from wastewaters, *J. Hazard. Mater.*, **318**, pp 631–40.

[49] El Alouani M, Alehyen S, El Achouri M and Taibi M Preparation, Characterization, and Application of Metakaolin-Based Geopolymer for Removal of Methylene Blue from Aqueous Solution, 2019.

[50] Sarkar C, Basu J K, and Samanta A N 2017 Removal of Ni2+ ion from waste water by Geopolymeric Adsorbent derived from LD Slag, *J. Water Process Eng.*, **17**, 237–44.

[51] Sarkar C, Basu J K and Samanta A N 2018 Synthesis of mesoporous geopolymer powder from LD slag as superior adsorbent for Zinc (II) removal, *Adv. Powder Technol.*, **29**(5):1142–52.

[52] Al-Essa K 2018 Heavy Metals Adsorption from Aqueous Solutions onto Unmodified and Modified Jordanian Kaolinite Clay: Batch and Column Techniques, *Am. J. Appl. Chem.*, **6**(1):p. 25.

[53] Wang L Li S and Zhu Z 2006 Geopolymeric adsorbents from fly ash for dye removal from aqueous solution,” *J. Colloid Interface Sci.*, **300**, no. (1):52–9.

[54] Novikova L A et al., 2019 Adsorption of Formaldehyde from Aqueous Solutions Using Metakaolin-Based Geopolymer Sorbents,” *Prot. Met. Phys. Chem. Surfaces*, **55**(5):864–71.

[55] Hashemian S, Saffari H and Ragabion S 2015 “Adsorption of cobalt(II) from aqueous solutions by Fe3O4/bentonite nanocomposite,” *Water. Air. Soil Pollut.*, **226**(1).

[56] Chang Y C and Chen D H 2005 Preparation and adsorption properties of monodisperse chitosan-bound Fe3O4 magnetic nanoparticles for removal of Cu(II) ions, *J. Colloid Interface Sci.*, doi: 10.1016/j.jcis.2004.09.010.

[57] S. Hashemian 2010 MnFe 2 O 4/bentonite nano composite as a novel magnetic material for adsorption of acid red 138,” *African J. Biotechnol.*, **9**(50):8667–71.

[58] Hashemian S 2011 Removal of acid red 151 from water by adsorption onto nano-composite MnFe2O4/kaolin,” *Main Gr. Chem.*, **10**(2):105–14.

[59] Kalyani S, Krishnaiah A and Boddu V M 2007 Adsorption of divalent cobalt from aqueous solution onto chitosan-coated perlite beads as biosorbent, *Sep. Sci. Technol.*, doi: 10.1080/01496390701511457.

[60] Oliveira L C A, Rios R V R A, Fabris J D, Sapag K, Garg V K and Lago R M 2003 Clay-iron oxide magnetic composites for the adsorption of contaminants in water, *Appl. Clay Sci.*, doi: 10.1016/S0169-1317(02)00156-4.

[61] Üzüm Ç, Shahwan T, Eroğlu A E, Hallam K R, Scott T B, and Lieberwirth I 2009 Synthesis and characterization of kaolinite-supported zero-valent iron nanoparticles and their application for the removal of aqueous Cu2+ and Co2+ ions,” *Appl. Clay Sci.*, doi: 10.1016/j.clay.2008.07.030.

[62] Vereš J, Orollová Z, Mockovčiaková A, Jakabský Š and Bakalár T 2009 Removal of nickel by natural and magnetically modified bentonite,” in *Water treatment technologies for the removal of high-toxicity pollutants*, Springer, pp. 289–294.

[63] Zhang G, Qu J, Liu H, Cooper A T and Wu R 2007 CuFe2O4/activated carbon composite: a novel magnetic adsorbent for the removal of acid orange II and catalytic regeneration, *Chemosphere*, **68**(6):1058–66.

[64] Kalhori E M, Al-Musawi T J, Ghaframani E, Kazemian H and Zarrabi M 2017 Enhancement of the adsorption capacity of the light-weight expanded clay aggregate surface for the metronidazole antibiotic by coating with MgO nanoparticles: Studies on the kinetic, isotherm, and effects of environmental parameters, *Chemosphere*, **175**, pp. 8–20, 2017.

[65] Medpelli D, Sandoval R, Sherrill L, Hristovski K and Seo D-K 2015 Iron oxide-modified nanoporous geopolymers for arsenic removal from ground water,” *Resour. Technol.*, **1**(1):19–27.


[66] Putra E K, Pranowo R, Sunarso J, Indraswati N and Ismadji S 2009 Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: Mechanisms, isotherms and kinetics, *Water Res.*, 43(9):2419–30,

[67] A. B. Dukić *et al.*, “Simultaneous removal of Pb2+, Cu2+, Zn2+ and Cd2+ from highly acidic solutions using mechanochemically synthesized montmorillonite-kaolinite/TiO2 composite,” *Appl. Clay Sci.*, 103, pp. 20–7, 2015