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Current Progress on Porous Geopolymers for Adsorption of Heavy Metals

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Abstract

Water resources are continuously contaminated by a variety of pollutants, from which heavy metals can be considered as a high-risk pollutant for the environment and human health. One of the most extensively used techniques for removal of heavy metals from wastewater is adsorption. This paper reviews the most recent literature on porous geopolymer adsorbent for heavy metal removal. In particular, fabrication methods and future perspectives have been investigated besides the related up-to-date researches. The overall results have indicated promising potential of porous geopolymer, which can mainly be attributed to its comparable adsorption capacity with respect to other adsorbents as well as its low cost and environmentally friendly fabrication process. However, since literature studies have generally conducted with the use of synthetic wastewater in batch systems, more research is needed on real wastewater with continuous processes in order to ascertain its performance.

Keywords: Adsorption, Geopolymer, Heavy metals, Pollutants, Porous geopolymer.

1. INTRODUCTION

Rapid and continuous industrialization has resulted in some serious detrimental effects on the environment including the contamination of clean water resources. There is a variety of pollutants such as heavy metals, dyes, pharmaceuticals, surfactants, pesticides, personal care products and others. From these, heavy metals are considered as a high-risk pollutant which can threaten the environment and human health. Heavy metals can be defined as inorganic elements with densities greater than 5 g/cm^3. They are mainly classified into two categories, namely essential and non-essential heavy metals [1], [2].

Essential heavy metals such as Cu, Zn, Fe, Co and Mn are usually harmless at low concentration and required for various biological processes in living organisms. On the other hand, non-essential heavy metals comprising of Pb, Cd, Cr, As and Hg are generally categorized as hazardous even in trace amounts mainly due to their high toxicity level and bio-accumulation characteristic in food chains [2]. Though a few approaches attempted, adsorption can be regarded as the most extensively used technique to remove heavy metals from wastewater owing to its simplicity, low cost and high efficiency. From a large number of adsorbents, activated carbon is accepted as benchmark material because of primarily its unique adsorption efficiency attributed to its extremely large surface area and moreover its good stability and long durability. However, its high synthesis cost and difficulties in the regeneration process have forced researchers to look for lower-cost yet effective and environmentally friendly alternatives [1]–[3].

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One promising alternative could be the use of geopolymers for this purpose. Geopolymers can be basically defined as a three-dimensional aluminosilicate framework which is amorphous or semi-crystalline structure. Their preparation is based on alkaline activation of various silica and alumina rich raw materials and by-products including mostly metakaolin, coal fly ash and blast furnace slag and also natural alumina-silicates, biomass fly ash, red mud, etc. at ambient or slightly elevated temperatures [3], [4]. Since geopolymers have numerous promising properties as cement replacement material in terms of economic, environmental and technical benefits, a considerable body of literature has been focused on their utilization potential in construction industry. Furthermore, geopolymers have recently captured much attention especially on wastewater treatment for the removal of various organic and inorganic pollutants including heavy metals and dyes using different methods, mainly adsorption and also photo-degradation, encapsulation and immobilization [3]–[11].

In this study, current advancement on porous geopolymers have been reviewed as alternative adsorbent material for removal of heavy metals.

2. METHODOLOGY

The methodology used in this study is based on extensive literature research related to current porous geopolymer technology and its utilization potential as alternative adsorbent for removal of heavy metals. Within this scope, processing approaches used for the synthesis of porous geopolymers and interaction mechanism between geopolymer and heavy metal ions have been examined. Moreover, future perspectives have been interpreted by evaluating the results obtained from current literature studies.

3. GEOPOLYMER

The term "Geopolymer" was first introduced by Davidovits in the late 1970s. Geopolymers, which have also been referred to inorganic polymers in literature, can be defined as a negatively charged three-dimensional aluminosilicate framework in which alkali metal cations such as Na^+, K^+ and Ca^{2+} ions function as charge-balancing cations. They were actually intended as a binder material for fire resistance applications owing to their inorganic origin. Geopolymers are synthesized at often ambient or slightly elevated temperatures typically below 100 °C by activating various alumina-silicate rich raw materials and by-products with chiefly strong alkaline solutions, hydroxides and silicates of sodium and potassium, and rarely acidic route with the use of phosphoric acid. In literature, metakaolin, coal fly ash and granulated blast furnace slag have primarily been used as alumina-silicate precursors while biomass fly ash, bottom ash, waste glass, red mud, clays and sedimentary rock powder have also been indicated as materials with a promising potential [1]–[4], [12].

Geopolymers are formed through a process called geopolymerization which sequentially involves dissolution, gelation and polycondensation. In geopolymerization, strong alkali solution first dissolves aluminosilicate precursor to form free silica (SiO_4) and alumina (AlO_4) tetrahedral units. Water then splits out and the tetrahedral units are alternatively linked to polymeric precursors by sharing of oxygen atoms. Depending on mainly Si/Al molar ratio, geopolymers with amorphous or semi-crystalline network structures could have different molecular units or chemical groups. The most commonly encountered molecular units in geopolymers are polysialate (-Si-O-Al-O-), polysialate-siloxo (-Si-O-Al-O-Si-O-) and polysialate-disiloxo (-Si-O-Al-O-Si-O-Si-O-) [1], [2], [13], [14].

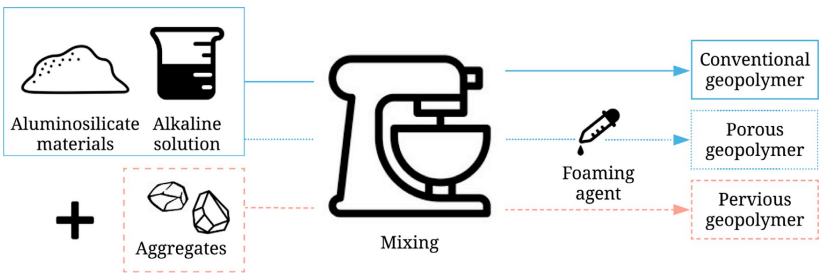

Figure 1. Schematic diagram of geopolymer fabrication: conventional, porous and pervious [2]

Figure 1 shows the fabrication process of the three main types of geopolymer, namely conventional, porous and pervious geopolymer [2]. Conventional geopolymer adsorbent is usually prepared at temperature ranging from 20-105 ºC with the use of mostly metakaolin and coal fly ash as aluminosilicate precursors and sodium-based alkaline activators, NaOH and Na_2SiO_3. Pervious geopolymer, which have also been referred to pervious concrete due to its aggregate inclusion, have numerous application areas, which can be attributed to its lightweight and permeable characteristics, such as acoustic and thermal insulation materials, bed materials for vegetation, solid-liquid separation and water purification. Pervious geopolymer could have a promising potential mainly due to its recently discovered water purification ability. Porous geopolymers containing high volume of voids or pores are produced by modifying conventional geopolymers [2]. The detailed information about porous geopolymer, which is the main topic of this study, was given in the following section.

4. POROUS GEOPOLYMERS

Porous geopolymer can be considered as a modified conventional geopolymer with a high volume of porosity that has been intentionally introduced. In literature, porous geopolymer generally comprises of pores with sizes ranging from nanometers up to millimeters and has total pore volumes varying in the range of 30-90%. Since porous geopolymers have much more available binding sites as an adsorbent compared to conventional geopolymers due to their higher porosity, they are no longer restricted to be used in powdered form. Instead, porous geopolymers can be produced with different shapes, such as spherical or monolith which are easier to retrieve after they are exhausted [2]. Numerous processing approaches have been developed for the synthesis of porous geopolymers, mainly including direct foaming, replica method, sacrificial filler/template method, additive manufacturing, fast microwave foaming and others [2], [15], [16].

4.1. Direct Foaming Method

Figure 2 illustrates the typical direct foaming process for the production of porous geopolymer, which is also widely used for porous ceramics and lightweight concrete fabrication [15]. Due to mainly its simplicity, direct foaming, either chemically or mechanically, is probably the most widely and commonly used foaming approach, providing microporous network in the hardened matrix [2]. In particular, the geopolymer foam is obtained by introducing or generating gas at room temperature in the wet slurry which is then set and cured at a slightly higher temperature. Gas is usually generated from the decomposition of a foaming agent added [15]. The most widely used foaming agent in literature studies has been by far hydrogen peroxide. The other common materials are metallic Al and Si powders. Moreover, Zn powder, silica fume, sodium perborate, sodium dodecyl benzene sulfonate (SDBS), lightcrete, sodium hypochlorite, sodium bicarbonate, commercial air entraining agent, silicon carbide and foam have also been tried in researches for this purpose [2], [15]. However, the wet foam produced is unstable, resulting in irregularly sized large pores and reducing microstructural uniformity and performance of final materials. In order to avoid this, some additives, such as SDBS, sodium dodecyl sulfate (SDS), oleic acid, calcium stearate, octyl sulfobetaine, lightcrete and glutin are usually added in combination with foaming agents [15].

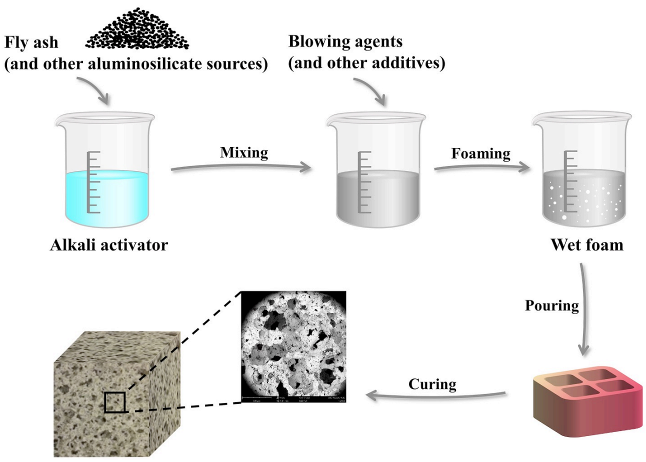

Figure 2. The process flow chart for the direct foaming method [15]

4.2. Sacrificial template method

As seen from Figure 3, in sacrificial template method, aluminosilicate sources are first mixed with a sacrificial template filler, generally polylactic acid to obtain a filler/geopolymer composite material, followed by heat and/or alkali treatments to remove filler, creating a porous geopolymer [15].

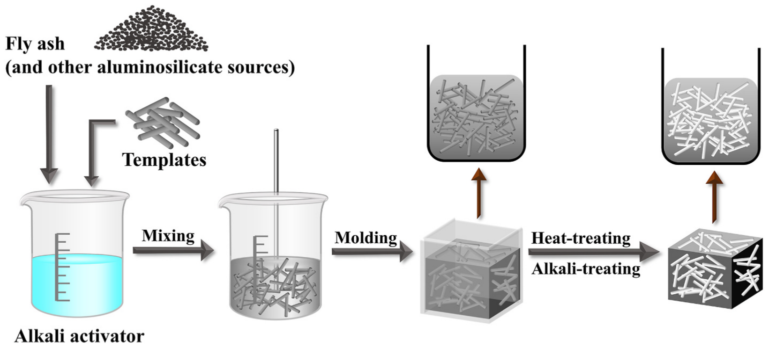

Figure 3. The process flow chart of the sacrificial template method [15]

4.3. Additive manufacturing method

Additive manufacturing or direct ink writing method is new and promising technology to produce porous materials. Additive manufacturing (3D printing) has recently received considerable attention owing to its ability to prepare complex structures with controllable pore size and pore distribution [15].

4.4. Fast microwave foaming method

In order to reduce curing time and increase geopolymerization efficiency, some researchers have proposed microwave foaming method for synthesizing porous geopolymers. Instantaneous and very fast heating in combination with easy control make microwave energy an innovative tool. In addition, in microwave heating, heat is directly transferred to the material through the interaction with the electromagnetic field at the water-molecule level, providing quick evaporation of water in the entire body. This results in a foam structure within the object in a very short time compared to conventional curing, which is conducted in an oven at 20-90 ^oC for approximately 24-48 h [15].

4.5. Embedding lightweight/porous fillers method

Embedding of lightweight or porous fillers such as hollow spheres and porous particles in a geopolymeric matrix is another way to generate pores [15]. Since some fly ashes originally contain hollow spheres, namely cenosphere, there are also studies in literature conducted with fly ash cenosphere as lightweight and porous filler material embedded in metakaolin-based and combination of fly ash and granulated blast furnace slag-based geopolymers to obtain a lightweight composite material with low thermal conductivity [17]–[19]. In addition, simultaneous introduction of gas by direct foaming with H_2O_2 and calcium stearate and incorporation of hollow glass microspheres has also been studied to produce a lightweight fly ash-based foam geopolymers with ultra-low thermal conductivity and relatively high strength [20].

4.6. Synthesis of porous geopolymer spheres by suspension solidification method

Unique characteristics of porous geopolymers have motivated researchers to study their utilization potential as an adsorbent on treating wastewater. With respect to powders and bulk-type adsorbents, spheres have various feasible characteristics such as easy handling, improved simplicity and efficiency of the process and higher alkali release ability. Similar to bulk-type porous geopolymers, several ways have been proposed for porous geopolymer spheres including suspension solidification method, direct molding method calcium chloride solution gel method [15]. Figure 4 illustrates schematic representation of porous geopolymeric spheres by suspension solidification method [21].

5. POROUS GEOPOLYMER ADSORBENT FOR HEAVY METAL REMOVAL

Heavy metal removal by geopolymers generally takes place through adsorption process, in which metal cation adsorbates are adhered onto the available binding sites of geopolymer adsorbent [2]. Table 1 summarizes the most recent literature studies conducted with porous geopolymer adsorbents for the removal of different heavy metal ions. As seen in Table 1, porous geopolymers have been recently applied for the adsorption of mainly lead and copper and also cadmium, mercury and nickel. Direct foaming and traditional and modified suspension solidification approaches have currently been used as major methods for the fabrication of porous geopolymers with a variety of size and shape, mostly sphere and monolith. Hydrogen peroxide has been the most widely used blowing agent, which is usually applied in combination with sodium dodecyl sulfate. Overall results obtained in these studies have suggested that porous geopolymer can be a promising adsorbent material for the removal of heavy metals from the solutions mainly due to its low cost, high adsorption capacity and environmentally friendly production process [10], [11], [21]–[27].

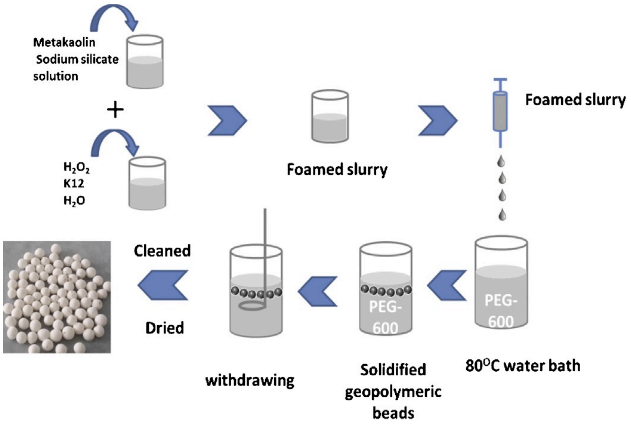

Figure 4. Schematic representation of porous geopolymeric spheres by suspension solidification method [21]

Table 1. Heavy metal removal by porous geopolymer

Precursor	Geopolymer characteristics: Production method	Blowing agent	Shape	Surface area (m^2/g)	Heavy metal ion	Operating conditions: Initial metal conc. (mg/L or ppm)	Adsorbent dosage (g/L)	pH	Uptake efficiency (%)	Adsorp. capacity (mg/g)	Ref.
VA and RHA	EPF	RHA	Monolith (Cylindrical disk)	27.88	Pb^{2+} Cd^{2+} Hg^{2+}	10	0.08	6	-	312.5 243.9 232.6	[22]
FA and MK	DF-DM	H_2O_2	Sphere	54.76	Ni^{2+}	800	-	5	67.1	19.41	[27]
CGFA, SS and MK	DF-MP	H_2O_2	Sphere	9.73	Pb^{2+}	90	1.5	5-6	99.9	59.31	[26]
FA and MK	DF-DM	H_2O_2	Sphere	54.76	Cu^{2+}	2000	-	5	15.6	37.9	[25]
MK with Al and Ch	SSM	H_2O_2/ SDS	Sphere	230	Pb^{2+}	-	-	5	-	142.7	[24]
MK and BFA	DF	H_2O_2	Monolith (Cylindrical disk)	-	Pb^{2+}	50	-	5	-	6.34	[11]
FA and IOT	DF	H_2O_2	Monolith (Cube)	-	Cu^{2+}	100	3	5-6	90.7 (pH5)	113.4 (pH6)	[10]
MK	SSM	SDS	Sphere	53.95	Pb^{2+} Cu^{2+}	100	1.5	5	68.4 53.25	45.6 35.5	[23]
MK	SSM	H_2O_2/ SDS	Sphere	53.95	Cu^{2+}	50	1.5	5	-	52.63	[21]

Al: Alginate, BFA: Biomass fly ash, Ch: Chitosan, CGFA: Coal gasification fly ash, DF: Direct foaming, DM: Direct molding, EPF: Embedding porous filler, FA: Fly ash, MK: Metakaolin, MP: Mechanical pelletization, RHA: Rice husk ash, SDS: Sodium dodecyl sulfate, SS: Steel slag, SSM: Suspension solidification method, VA: Volcanic ash.

6. FUTURE PERSPECTIVES

Literature studies have pointed out the favorable potential of porous geopolymers as adsorbent especially for the removal of heavy metals and dyes. However, their performance should also be tested on other pollutants such as pharmaceuticals, oil and grease, phenolic compounds and micro-pollutants [1]. In addition, due to their negative surface charge at spontaneous pH conditions, which can be attributed to the aluminosilicate framework, geopolymers seems more suitable for the removal of cationic species in wastewater treatment. Although there are very few recent studies conducted on anionic dyes, mainly the necessity of very low pH values limits their usage [1], [4]. Since there are numerous anionic-based pollutants in wastewater, advanced geopolymer-composite hybrid materials should be fabricated in order to overcome these pollutants. Furthermore, future studies should also concentrate on increasing the selectivity of contaminants in multicomponent system, and more studies should be conducted with the use of real wastewaters and continuous process [1], [2].

7. CONCLUSION

This study has reviewed the current progress on porous geopolymers as adsorbent for the removal of heavy metals. Within this scope, processing approaches used for the synthesis of porous geopolymers have been covered in detail as well as the related most recent researches, which have been examined in terms of aluminosilicate precursors, geopolymer characteristics, operating conditions, removal efficiency of metals and adsorption capacity of geopolymers. Overall results obtained in the related literature have proposed that porous geopolymer can be a promising adsorbent material for the removal of heavy metals from the solutions mainly due to its low cost, high adsorption capacity and environmentally friendly production process. However, considering the limited literature on the topic, which have been conducted with synthetic wastewater in batch systems, further studies are required to ascertain its performance on real wastewater with continuous processes.

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