



Fly ash-based geopolymer for Pb removal from aqueous solution

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ABSTRACT

The aim of this work was to synthesis highly amorphous geopolymer from waste coal fly ash, to be used as an adsorbent for lead Pb(II) removal from aqueous wastewater. The effect of various parameters including geopolymer dosage, initial concentration, contact time, pH and temperature on lead adsorption were investigated. The major components of the used ash in the current study were SiO₂, Al₂O₃ and Fe₂O₃ representing 91.53 wt% of its mass. It was found that the synthesized geopolymer has higher removal capacity for lead ions when compared with that of raw coal fly ash. The removal efficiency increases with increasing geopolymer dosage, contact time, temperature, and the decrease of Pb²⁺ initial concentration. The optimum removal efficiency was obtained at pH 5. Adsorption isotherm study indicated that Langmuir isotherm model is the best fit for the experimental data than Freundlich model. It was found also that the adsorption process is endothermic and more favorable at higher temperatures.

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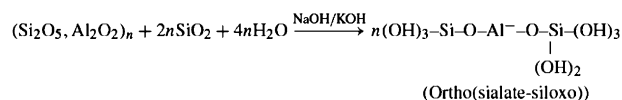
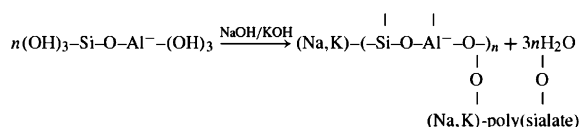
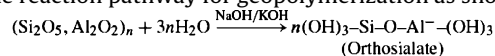
1. Introduction

The amount of fly ash released by factories and thermal power plants has been increased throughout the world. Therefore, the disposal of fly ash has become a serious environmental and economical problem [1,2]. In the past, fly ash was generally released into the atmosphere, but in recent decade pollution control measures require that it should be captured prior to release. Only about 20–30% of the generated fly ash is used, mainly as additive in cement and concrete and as filling material, and the rest is disposed off. Therefore, strategies to deal with this waste safely are required [3].

One of the most important approaches to deal with fly ash problem is to convert it to useful and applicable material [4]. It is known that fly ash contains appreciable quantities of aluminosilicates, which make it cheap and ready available source of Si and Al for the synthesis of zeolites and geopolymer materials [2,5,6]. Therefore, the synthesis of geopolymer binders will be a successful alternative to deal with fly ash waste, resulting in low-cost and environmentally friendly materials.

The synthesis of geopolymer is normally carried out by mixing aluminosilicate reactive materials with strong alkaline solutions (such as NaOH or KOH), then curing the mixture at temperatures between 20 and 100 °C [7,8]. Under such conditions aluminosilicates are dissolved rapidly into the solution to form free SiO₄ and

AlO₄ tetrahedral units. These units are then gradually split out with the development of reaction, and linked alternatively to yield polymeric precursors (–SiO₄–AlO₄–, or –SiO₄–AlO₄–SiO₄–) by sharing all oxygen atoms between two tetrahedral units, and thereby forming monolithic like geopolymer products (named polysialates as suggested by Davidovits [9,10]) [11]. Davidovits [9] has proposed the reaction pathway for geopolymerization as shown below:



As shown in the reaction pathway above, the positive ions (such as Na⁺ or K⁺) must present in the frame work cavities to balance the negative charge of Al [9].

So, the formation of geopolymeric materials follows much the same route as that for most zeolites. This includes dissolution and formation of mobile precursors, partial orientation of mobile precursors as well as the partial restructuring of the alkali polysilicates, and re-precipitation to form an inorganic polymeric structure [4,12]. However, during geopolymerisation, once the alumino-silicate powder is mixed with the alkaline solution a paste forms and quickly transforms into a hard geopolymer. Therefore,

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there is no sufficient time and space for the gel or paste to grow into a well crystallized structure; this is the fundamental difference between zeolites and geopolymers. After shorter setting and hardening time, geopolymers, with tightly packed polycrystalline structure, are formed exhibiting better mechanical properties than zeolites which have lower density and cage-like crystalline structure [13].

Although synthesis of geopolymer is not a new concept, the application of this technology, to treat waste materials, is relatively recent. Geopolymers have unique properties which make them interesting subject for investigation. The main properties of geopolymers are: quick compressive strength development, low permeability, resistance to acid attack and fire; fast setting, good resistance to freeze-thaw cycles, and tendency to drastically decrease the mobility of most heavy metal ions contained within the geopolymeric structure. Such properties make them interesting structural products, such as concrete replacements in various environments, and immobilization systems for heavy metal containment [5,12,14–17].

Conversion of fly ash to an amorphous aluminosilicate adsorbent (geopolymer) has been investigated under different conditions and was paid great attention as a potential material for removal of Cd, Ni, Pb(II), Cu(II), phosphate, NO_x , boron, fluoride, radionuclide of ^{137}Cs and ^{90}Sr , and dyes [1].

Factors that affect the adsorption capacity such as ash composition [4,18], dosage of adsorbent [18–20], effect of pH [19–22], effect of temperature [4,20,22,23], effect of contact time [19,20] and effect of initial concentration of contaminant [18,21,22] are of great concern by several investigators.

The main aim of this work is to synthesis highly amorphous geopolymer from coal fly ash, and to use the produced material as an adsorbent for removal of lead Pb(II) from aqueous solution. Adsorption of Pb(II) on synthesized geopolymer is studied as a function of the geopolymer dosage, lead initial concentration, contact time, pH and temperature. The adsorption isotherm is also studied and the thermodynamic parameters have been calculated.

2. Materials and experimental work

2.1. Materials

All chemicals used in this study were of analytical grade reagents. A 1000 ppm standard lead (Pb) solution was purchased from Merk®, while nitric acid and sodium hydroxide were obtained from Scharlau-Spain. Samples of coal fly ash were obtained from Al-Rajih Cement-Jordan plant. The samples were ground gently in a pestle and mortar and sieved for different particle size fractions. The particle size of $<45\ \mu\text{m}$ was selected for geopolymer synthesis. Similar particle size was used by Wang et al. [14]. Geopolymer bodies were then crushed and sized – reduced down to $200\ \mu\text{m}$ for further use [24].

2.2. Instrumentation

X-ray diffraction (XRD) analysis was performed using (SHIMADZU-XRD-6000) diffractometer, where scanning was done according to 2θ scanning range of $2.0\text{--}65.0^\circ$, continuously with $2.000^\circ/\text{min}$ scan speeds, and the receiving slit width was $0.30\ \text{mm}$. The chemical composition for both fly ash and geopolymer samples was obtained using X-ray fluorescence (XRF) spectrometer (SHIMADZU-XRF-1800). The concentrations of Pb(II) was determined using inductively coupled plasma (ICP) (SHIMADZU-ICPS-7510) under the following conditions: Radio frequency power = $1.2\ \text{kW}$, coolant gas flow = $14.0\ \text{L}/\text{min}$, plasma gas flow = $1.20\ \text{L}/\text{min}$ and carrier gas flow = $0.70\ \text{L}/\text{min}$.

pH-meter model (WTW) was used for pH measurements, and was adjusted using two buffer solutions (potassium hydrogen phthalate at $\text{pH} = 4.0$ and potassium di-hydrogen/di-sodium hydrogen phosphate at $\text{pH} = 7.0$). During this study, the mass measurement of samples were carried out using (AND) analytical balance model (HM-200) to the nearest of $0.10\ \text{mg}$. (THP-72) type shaker equipped with a digital thermostat was used to undergo batch adsorption experiments.

2.3. Synthesis of geopolymer

Certain amounts of fly ash were mixed with $14\ \text{M}$ NaOH solution using a mass ratio of 1.25. The choice of this ratio was based on previous studies [2], where it was found that lower fly-ash:NaOH ratio results in lower adsorption capacity and the best geopolymer adsorption capacity was obtained when this ratio was higher than 1.2. Geopolymer paste then started to form, which was mixed for 5–10 min to give complete homogenization. The mixtures were put in polypropylene cylinders ($30\ \text{mm} \times 60\ \text{mm}$) which were half-filled and vibrated for 30 s using ultrasonification, and then fully-filled and vibrated for 30 s [3]. The vibration of geopolymer paste aimed to de-foam geopolymer body. On the other hand, ultrasonification process enhances the dissolution of Al–Si material (fly ash) in the alkaline solution [3]. The mixtures were then pre-cured for 24 h at room temperature. This process induces significant dissolution of silica and alumina from fly ash and formation of a continuous matrix phase, increasing, therefore, the homogeneity of the geopolymeric materials.

The paste was then poured in a cylindrical container which was closed for curing at a temperature of 105°C for 24 h in an oven. The geopolymer sample was removed from the oven and kept at room temperature for 3 days [23]. This curing process was found to be beneficial to develop the strength of the geopolymer [23]. Geopolymer bodies were washed at least 3 times to remove the excess sodium hydroxide, and then crushed and sized – reduced down to $200\ \mu\text{m}$.

2.4. Adsorption of lead on geopolymer

2.4.1. Effect of geopolymer dosage

A $50.0\ \text{ml}$ of $100\ \text{ppm}$ Pb(II) solutions were added to variable geopolymer masses at a fixed pH (5), temperature (25°C), and shaking time (120 min) as shown in Table 1. For each dose, equilibrium concentration was measured and the uptake percentage and adsorption capacity were calculated.

2.4.2. Effect of pH

A $50.0\ \text{ml}$ of $100\ \text{ppm}$ Pb(II) solution was shaken for 120 min at a temperature of 25°C , with a constant amount of geopolymer ($0.07\ \text{g}$) and at different pH values (3.0–5.0). The pH was adjusted either with the addition of diluted nitric acid (HNO_3) or sodium hydroxide (NaOH). For each pH value, equilibrium concentration was measured, then the uptake percentage and adsorption capacity were calculated.

2.4.3. Effect of contact time

In order to study the effect of contact time on the adsorption of Pb(II) ions by geopolymer, $50.0\ \text{ml}$ aliquot of $100\ \text{ppm}$ Pb(II) solutions at pH 5 was added to $0.07\ \text{g}$ geopolymer, the solution was then shaken for different periods of time (5–180 min) at a temperature of 25°C . The uptake percentage and adsorption capacity were determined for each contact time.

2.4.4. Effect of temperature

Effect of temperature on Pb(II) adsorption was evaluated at temperatures of 25, 35, and 45°C . The other parameters were kept

Table 1
Summary of adsorption experiments conditions.

| Investigated parameter | Temperature (°C) | pH | Geopolymer dose (g) | Contact time (min) |
|------------------------|------------------|----|---------------------|--------------------|
| Geopolymer dosage | 25 | 5 | 0.03 | 120 |
| | | | 0.05 | |
| | | | 0.07 | |
| | | | 0.08 | |
| | | | 0.10 | |
| Contact time | 25 | 5 | 0.07 | 5 |
| | | | | 10 |
| | | | | 15 |
| | | | | 30 |
| | | | | 60 |
| | | | | 120 |
| | | | | 160 |
| pH | 25 | 1 | 0.07 | 120 |
| | | 2 | | |
| | | 3 | | |
| | | 4 | | |
| | | 5 | | |
| | | 6 | | |
| Temperature | 25 | 5 | 0.07 | 120 |
| | 35 | | | |
| | 45 | | | |

constant (Pb(II) = 100 ppm, geopolymer dosage = 0.07 g, pH = 5, and contact time = 120 min). For each temperature, equilibrium concentration was measured, then the uptake percentage and adsorption capacity were calculated.

2.4.5. Effect of initial concentration

The effect of initial concentration on the adsorption of Pb(II) ions by geopolymer was investigated employing different concentrations of Pb(II) ranging from 10 to 140 ppm at pH values (3, 4, and 5) and geopolymer dosage of (0.07 g), the solution was then shaken for 120 min at a temperature of 25 °C. For each initial concentration, equilibrium concentration was measured, then the uptake percentage and adsorption capacity were calculated.

2.5. Adsorption isotherm

The study of Pb(II) adsorption isotherms on the synthesized geopolymer were carried out using batch equilibrium technique according to the following procedure; 50.0 ml of Pb(II) solutions (10–140 ppm) was added to a fixed mass of geopolymer (0.07 g) at different pH values (3, 4, 5) and temperatures (25, 35, 45 °C). The mixture was shaken at constant temperature for a fixed period of time. The solution was then filtered and the concentrations of Pb(II) before and after adsorption were measured using ICP. Based on the experimental results many indicators were determined and two isotherm models (Langmuir and Freundlich) were examined using the obtained data.

2.6. Theoretical calculations

2.6.1. Removal efficiency and distribution coefficient (K_d)

Removal efficiency (%) was calculated using the following equation:

$$\text{Removal efficiency}(\%) = \frac{C_0 - C_{eq}}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration of Pb (ppm), C_{eq} is the residual concentration of Pb ion in solution after equilibrium (ppm).

Distribution coefficient (K_d) is a standard parameter in the assessment of the physiochemical behavior of metal ion between solid and liquid phases. It can be used to evaluate the sorption and retention of the metal ion in geopolymer. K_d was calculated using

the following equation [25].

$$K_d = \frac{\text{Conc. of metal ion sorbed or retained (mg/L)} \times V}{\text{Conc. of metal ion in solution (mg/L)} \times m} \quad (2)$$

$$K_d = \frac{(C_0 - C_{eq}) \times V}{C_{eq} \times m} \quad (3)$$

where V is the volume of the solution (L) and m is the mass of geopolymer (g).

2.6.2. Determination of uptake capacity

The adsorption isotherms were determined for Pb(II), at different pH values and different temperatures in the concentration range of 10–140 mg/L.

The amount of metal ion uptake by geopolymer can be obtained according to the following expression [25]:

$$q = \frac{(C_0 - C_{eq}) \times V}{m} \quad (4)$$

where q is the amount of metal ion uptake by geopolymer (mg (metal)/g geopolymer).

2.6.3. Langmuir isotherm

The Langmuir isotherm has been used by various workers for the sorption study of a variety of compounds. The model assumes uniform energies of adsorption onto a surface and no transmigration of adsorbate in the plane of the surface [20]. There are many linear forms of the Langmuir isotherm. One of the most applied forms is given by the following equation [26]:

$$\frac{1}{q} = \frac{1}{q_m K_L} \frac{1}{C_{eq}} + \frac{1}{q_m} \quad (5)$$

K_L is the Langmuir equilibrium constant that is related to the heat of adsorption and q_m is the maximum monolayer sorption capacity. If Langmuir equation is applicable, a plot of $1/q$ against $1/C_{eq}$ should give a straight line with a slope of $(1/(q_m K_L))$ and an intercept of $(1/q_m)$. Applicability of Langmuir model was investigated under different temperatures (25, 35, and 45 °C) and pH values of (3, 4, and 5). Non-linear regression using Datafit® software was used to find the parameters of the model.

2.6.4. Freundlich isotherm

The Freundlich isotherm is an empirical model that can be used for non ideal sorption process, which involves heterogeneous adsorption surface and active sites with different energies. It can be expressed by the following equation [27]:

$$q = K_F C^{1/n} \quad (6)$$

where q is the quantity of the solute adsorbed per unit weight of adsorbent, C is the equilibrium concentration of the adsorbing compound, and K_F ($\text{mg}^{1-(1/n)} \text{g}^{-1} \text{L}^{1/n}$) represents the adsorption capacity when metal ion equilibrium concentration equals to 1, and n represents the degree of dependence of adsorption on equilibrium concentration [25]. When this equation is expressed in logarithmic form, a linear relationship is obtained.

$$\log q = \log K_F + \frac{1}{n} \log C \quad (7)$$

When the data are plotted as $\log q$ vs. $\log C$, the intercept equals to $\log K_F$ and the slope is $1/n$. Applicability of Freundlich model was investigated under different temperatures (25, 35, and 45 °C) and pH values of (3, 4, and 5).

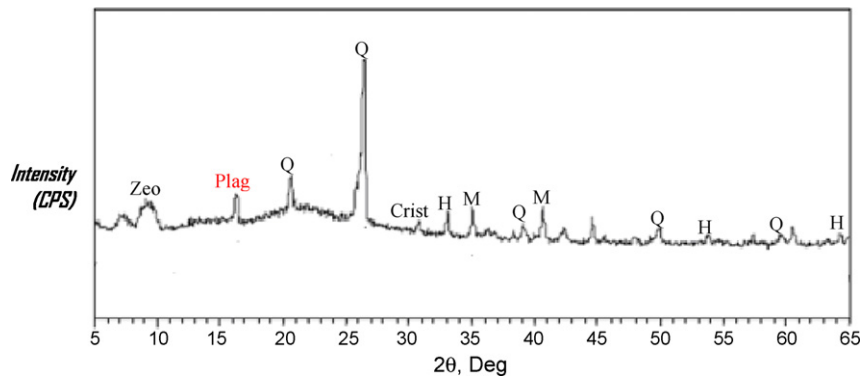


Fig. 1. XRD pattern of raw fly ash (Q – quartz, H – hematite, M – mullite, Zeo – zeolite, Plag – plagioclase, Crist – cristobolite).

2.7. Thermodynamic study

The values of enthalpy (ΔH°) and entropy (ΔS°) of the adsorption process were calculated using the following equation [20].

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

where T is temperature in Kelvin, and R is the gas constant. When ($\ln K_d$) vs. ($1/T$) is plotted, the slope of the straight line will yield ($\Delta H^\circ/R$) and an intercept will be ($\Delta S^\circ/R$), thus ΔS° and ΔH° can be determined. The change in Gibbs free energy (ΔG°) was calculated using the following equation [20]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

3. Results and discussion

3.1. Characterization of fly ash samples

3.1.1. XRD characterization

The XRD pattern of fly ash is shown in Fig. 1. It was found that the fly ash sample consists of quartz as major mineral, hematite and mullite in considerable amounts, while zeolite, plagioclase and cristobolite are presented in trace amounts. More than 60% of fly ash content is amorphous; this amorphous component is the important part for fly ash reactivity and higher proportion amorphous equates to high reactivity [28].

After geopolymerization process, as illustrated in Fig. 2, the resulting geopolymer has amorphous phases. The XRD pattern of the geopolymer is different from that of the original fly ash. The sharp peaks, which are characteristics for quartz, hematite, mullite and other identified minerals (Fig. 1), have disappeared and broad band peaks appeared, as shown in Fig. 2, which are

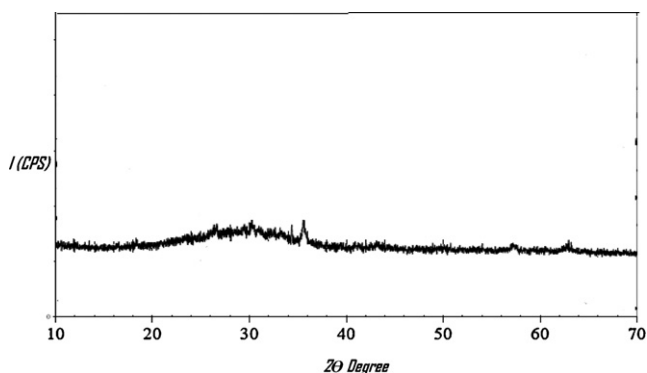


Fig. 2. XRD pattern fly ash-based geopolymer.

characteristics for amorphous materials. This indicates the dissolution of fly ash glass phases and the formation of amorphous structure in the geopolymer. Most of the crystalline phase of raw fly ash disappeared and the amorphous phase, which is characteristic of a geopolymer, is apparent. This indicates that the crystalline aluminum silicate has been geopolymerized to amorphous geopolymer during synthesis.

3.1.2. XRF analysis

The chemical composition of fly ash obtained by XRF technique is presented in Table 2. It is apparent that raw fly ash mainly consists of silica, alumina with some iron, calcium and magnesium oxides. It is shown that SiO_2 , Al_2O_3 and Fe_2O_3 represent 91.53 wt% of the sample mass, so it can be classified as class F fly ash according to the American Society for Testing Materials (ASTMC618) [1]. After geopolymerization, the content of sodium and the loss on ignition (L.O.I) increased considerably, although, the treated ash was washed thoroughly with distilled water and dried at 105°C . This indicates the incorporation of sodium and hydroxyl group within the structure of geopolymer as a result of geopolymerization process. This explains the reduction of SiO_2 and Al_2O_3 content in the geopolymer when compared with their content in the raw fly ash.

Many fly ash sources contain considerable amount of Ca, which has an adverse effect on the process of converting fly ash to geopolymer, since the presence of calcium in the fly ash affects the process of geopolymerization by providing extra nucleation sites for precipitation of dissolved species. As a result, calcium content in the current fly ash sample (1.73%) enhances its usage for environmental applications [29]. However, when the CaO content is high, the microstructural porosity decreases and the resulting formation of amorphous structure Ca–Al–Si gel strengthens the final product [13,17,30,31].

Table 2
The chemical composition coal fly ash.

| Compound (%) | Raw ash | After geopolymerization |
|-------------------------|---------|-------------------------|
| SiO_2 | 50.73 | 39.90 |
| Al_2O_3 | 28.87 | 19.70 |
| Fe_2O_3 | 11.93 | 7.50 |
| CaO | 1.73 | 2.43 |
| MgO | 1.39 | 1.13 |
| K_2O | 0.74 | 1.08 |
| Na_2O | 0.30 | 11.72 |
| TiO_2 | 1.41 | 0.50 |
| SO_3 | 0.35 | 0.25 |
| L.O.I | 2.53 | 14.69 |

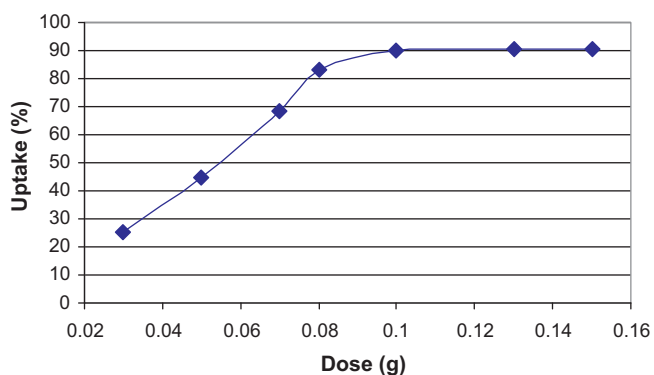


Fig. 3. Effect of adsorbent dosage on Pb uptake (100 ppm concentration, 25 °C, pH = 5.0, and contact time = 120 min).

3.2. Pb(II) uptake by raw coal fly ash and synthesized geopolymer

The lead removal efficiency of both raw coal fly ash and the synthesized geopolymer was compared at the given conditions: pH = 5; $C_0 = 100$ ppm; and $t = 120$ min. It was found that the removal efficiency for both raw fly ash and the geopolymer was 39.87% and 90.6%, respectively. Although fly ash is the main constituent of the geopolymer system, this result indicates that the synthesized geopolymer has the superior advantage in increasing the percent of metal ion uptake when comparing with raw fly ash. Ash contains some impurities which can block the matrix pores and hence retard the target solute from being adsorbed efficiently. However, the synthesized geopolymer has a well defined pore size distribution and its surface area is higher [14]. Furthermore, this surface is enriched with the functional groups during activation by strong base. Similar results are presented by Wang et al. [14], who found that fly ash produces little adsorption capacity for Cu^{2+} while geopolymer exhibits much higher adsorption capacity (more than 900 times). This variation in adsorption capacity is attributed to the higher surface area (7 times) and pore volume of geopolymer (14 times) where the larger pore structure is favorable to metal adsorption.

3.3. Parameters affecting Pb adsorption

3.3.1. Effect of geopolymer dosage

The effect of geopolymer dosage on the adsorption of Pb(II) is shown in Fig. 3. The adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbed material. The results show that the adsorption efficiency increased from 50.7 to 97.1% as the dose increases from 0.03 g (0.6 g/l) to 0.1 g (2.0 g/l), while the adsorption capacity decreased from 84.5 to 48.55 mg/g for the same doses, respectively. Higher increase was noticed with lower doses while insignificant increase was noticed when higher doses (>0.08 g) were used. This increase is explained by the increase in the surface area and the available adsorption sites of geopolymer samples. With increasing geopolymer content, the available sites for binding Pb(II) ions increases and thereby enhances the adsorption from solution to geopolymer [25].

The optimum weights which achieve the higher adsorption percentage of Pb(II), was 0.08 g (1.6 g/l). Cetin and Pehlivan [19] found that the rate of removal of metal ions (Zn) has increased with increasing of adsorbent dose. Gupta and Ali [20] used fly ash of sugar industry and found that the dose of 10 g/l resulted in adsorption capacity of 3.8 mg/g. However, in the current study a dosage of 0.07 g was used because the residual concentration of Pb at higher dosage was close to the detection limit of the ICP instrument.

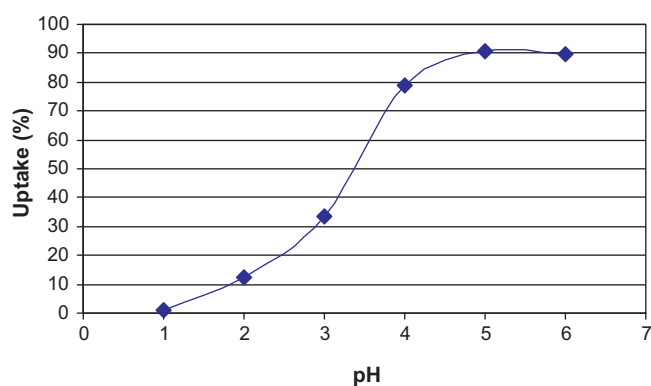


Fig. 4. Effect of pH on Pb uptake (100 ppm concentration, 25 °C, dose = 0.07 g, and contact time = 120 min).

3.3.2. Effect of pH

The effect of pH value on metal uptake was studied and the sorption capacity profile of the geopolymer is shown in Fig. 4. Result indicates that the adsorption efficiency increases from 1% to 90.66% as pH increases from 1 to 5, while it decreases slightly (89.8%) at pH 6. This indicates the zero point of charge is about pH 5.

At low pH values, there is an excess of H_3O^+ ions in the solution, which make a competition between the positively charged hydrogen ions and Pb^{2+} ions for the available adsorption sites on the negatively charged geopolymer surface. As the pH increases, the competition between protons and Pb(II) for surface sites will decrease and Pb^{2+} ion is the predominating species, which will attract to the surface of geopolymer by columbic forces. If pH value is greater than 5.0, lead hydroxide such as $Pb(OH)_3^{1-}$ begins to form resulting in the decrease of Pb(II) adsorption on geopolymer [25,32]. Gupta and Ali [20] found that the maximum uptake of lead and chromium took place at pH 6.0 and 5.0, respectively. Cetin and Pehlivan [19] found that the maximum adsorption of Zn(II) and Ni(II) occur at pH 4.0–5.0. Buasri et al. [33] found that the maximum lead removal by Natural Clinoptilolite occurred at pH 5. They found that metal adsorption decreased when pH was decreased from 7 to 2, due to competition with hydrogen ions. As pH increases, the concentration of the hydrogen ions, as competitors, decreases which leads to an increase of the amounts of sorbed metal. In general, the adsorption of most metal ions increases with the increase of pH up to a certain value, and then decreases with further increase in pH [1].

3.3.3. Effect of contact time

The time dependence behavior of Pb adsorption was measured by varying the equilibrium time between the adsorbate and adsorbent in the range of 5–180 min and the concentration of Pb(II) ions was kept 100 ppm at fixed geopolymer dosage (0.07 g) and pH 5. The results of these experiments are shown in Fig. 5.

It can be seen that the adsorption of Pb(II) metal ions on geopolymer increases with increase of contact time and reaches maximum value after 120 min, and thereafter it remains constant (plateau). A significant removal of Pb occurred within the first 30 min (80.24%) and slight change in terms of removal was noticed after 1 h. Gupta et al. [20] found that the equilibrium contact time for lead was 60 min. Similar results were obtained by Cetin and Pehlivan [19], where the maximum removal of Zn(II) and Ni(II) ions by fly ash was achieved after 1 h. It can be concluded that the removal of Pb(II) metal ions occurs quickly and 120 min shaking time is enough to achieve the adsorption equilibrium. Therefore, this contact time interval was used in all subsequent experiments. At this equilibrium time, the uptake percentage of Pb was 90.6%.

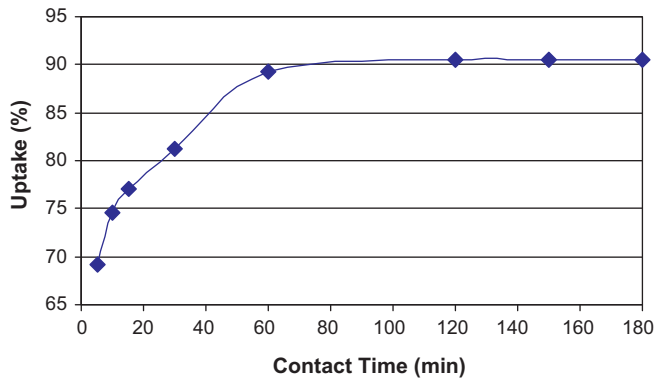


Fig. 5. Effect of contact time on Pb uptake (100 ppm concentration, 25 °C and dosage = 0.07 g, pH = 5).

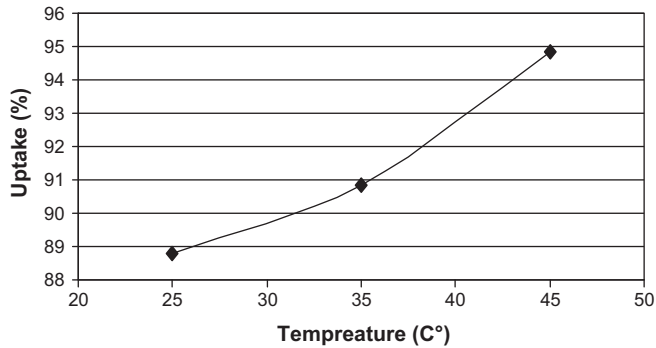


Fig. 6. Effect of temperature on Pb uptake (100 ppm concentration, pH = 5, contact time = 120 and dose = 0.07 g).

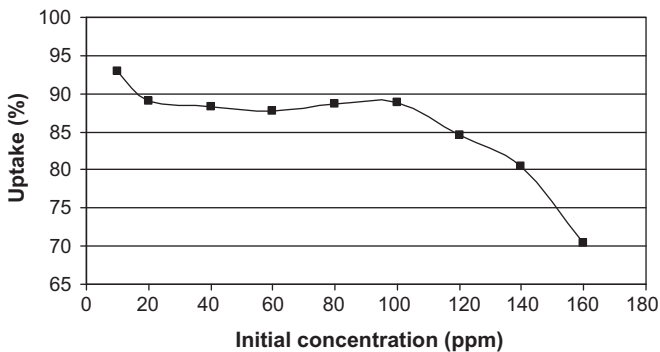


Fig. 7. Effect of the initial concentration on Pb uptake (°C = 25, pH = 5, dose = 0.07 g, contact time = 120 min).

3.3.4. Effect of temperature

The effect of temperature on the adsorption percentage is shown in Fig. 6. It can be noticed that the adsorption of Pb(II) metal ions on geopolymer increases with the increase of temperature. The uptake values increase from 63.42 to 67.75 mg/g as the temperature increases from 25 to 45 °C respectively. Several investigators concluded that the metals uptake is favored at higher temperatures [14,33]. Elevating the curing temperature increases the extent and rate of reaction, shown through an increase in porous structure, surface area, and pore volume which enhance adsorption process [14,34]. Additionally, high temperature inside the specimen can cause water vaporization and formation of micro-cavities thereby increasing adsorption capacity [6].

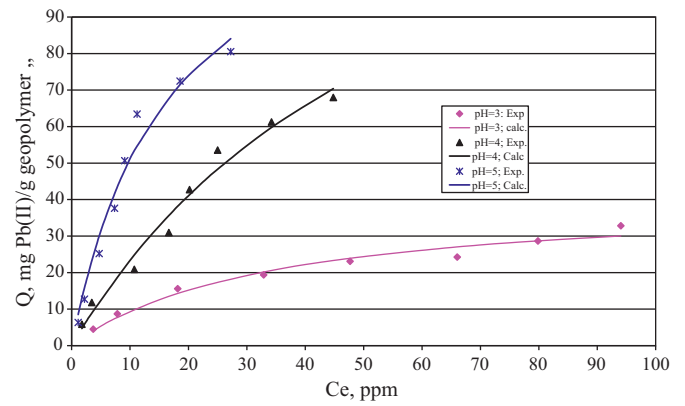


Fig. 8. Comparison between experimental and theoretical Langmuir values of Q as a function of Ce at different pH values and at a temperature of 25 °C.

3.3.5. Effect of initial concentration

Fig. 7 presents the adsorption efficiency of geopolymer at different initial Pb concentration. It can be seen that the removal efficiency will remain at high level (>80%) with initial concentration <140 mg/L. The efficiency decreases from 88.8% at 100 mg/L to 81% at 140 mg/L, while the uptake capacity increases from 63.421 to 81 mg/g for the same concentrations. With low initial concentration, the available pores in the adsorbent surface are sufficient to adsorb most of the metal ions, which had filled the possible available sites, so the adsorption efficiency increases to a certain level. As the initial concentration increases, the available pores become insufficient to adsorb further metal ions and much of ions still in suspension and no metal ions can be adsorbed. Several investigations have shown that the removal efficiency of heavy metals is concentration dependent and there is a decreasing trend with the increase of initial concentration [14].

3.4. Adsorption isotherms of geopolymer

3.4.1. Langmuir adsorption isotherm

The adsorption isotherms were determined for Pb(II), at different pH values and different temperatures in the concentration range from 10 to 140 mg/L. The uptake capacity (q) was calculated according to Eq. (4) and then the adsorption isotherms parameters (q_m and K_L) were calculated using Datafit® software.

The correlation coefficients were found to be between 0.97 and 0.99 for the conditions investigated ($T=25-45$ °C and $pH=3-5$). Since the values of R^2 for Langmuir isotherm for these conditions are very close to 1, monolayer adsorption is obtained and the process becomes highly favorable. The fitness of Langmuir isotherm for the adsorption process shows that the adsorption is homogenous and negligible interaction between adsorbed molecules [1]. The maximum adsorption capacity of geopolymer for Pb^{2+} was calculated under the experimental conditions as illustrated in Table 3. As shown in Table 3 the maximum adsorption capacity (q_m) increases as the temperature increases from 25 to 35 then drops slightly at 45 °C. Similarly, q_m increases considerably with the increase of pH from 3 to 4 then drops slightly at pH 5. On the other hand, the (K_L) values increase with increasing temperature.

Many investigators fitted adsorption process to Langmuir and Freundlich isotherm models, and found high correlation for both models [2,19,20,35].

The validity of Langmuir isotherm can be tested by comparing the theoretical adsorption capacity values calculated from Langmuir adsorption isotherm with those values obtained experimentally, as shown in Fig. 8 [27]. There is a strong compatibility between the experimental and calculated values, where the aver-

Table 3
Langmuir coefficients for different temperatures and pH values.

| T (°C) | pH=3 | | | pH=4 | | | pH=5 | | |
|--------|----------------|-----------------------|-----------------------|----------------|-----------------------|-----------------------|----------------|-----------------------|-----------------------|
| | R ² | q _m (mg/g) | K _L (L/mg) | R ² | q _m (mg/g) | K _L (L/mg) | R ² | q _m (mg/g) | K _L (L/mg) |
| 25 | 0.9700 | 40.76 | 0.0298 | 0.9773 | 166.55 | 0.0163 | 0.9719 | 134.95 | 0.0607 |
| 35 | 0.9677 | 45.79 | 0.0327 | 0.9808 | 183.605 | 0.0191 | 0.9875 | 150.57 | 0.0708 |
| 45 | 0.9818 | 45.52 | 0.0687 | 0.9831 | 182.41 | 0.0240 | 0.973 | 174.34 | 0.0931 |

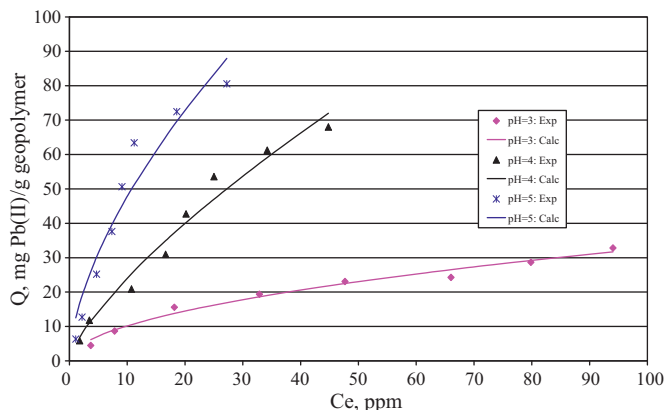


Fig. 9. Comparison between experimental and theoretical Freundlich values of Q as a function of C_e at different pH values and at a temperature of 25 °C.

age percentage of errors at initial concentration of 140 ppm are 6.6%, 1.4%, and 2.5% at pH value of 3, 4 and 5, respectively.

The dimensionless separation factor (R_L) was calculated from the Langmuir isotherm using the following equation [20]:

$$R_L = \frac{1}{1 + KC_{eq}} \quad (10)$$

where K is Langmuir adsorption constant; C_{eq} is equilibrium concentration at maximum adsorption capacity (q_m).

The values of R_L were found to be 0.377, 0.417 and 0.470 for temperature values of 25, 35 and 45 °C respectively. The value of $R_L < 1$ indicates a high and favorable adsorption process [20].

3.4.2. Freundlich adsorption isotherm

Freundlich adsorption isotherm was determined for Pb(II), at different pH values and different temperatures in the concentrations range from 10 to 140 mg/L. Uptake capacity (q) was calculated according to Eq. (6), then Eq. (7) was used as a linear form of Freundlich isotherm, where ($\log q$) was plotted against ($\log C$), which result in a straight line with a slope of ($1/n$) and an intercept of ($\log K_f$). Fig. 9 shows the compatibility between the experimental and calculated values where the average percentage of errors at initial concentration of 140 ppm are 2.9%, 3.2%, and 6.6% at pH value of 3, 4 and 5, respectively.

It was found that the correlation coefficients were between 0.935 and 0.989 as shown in Table 4. The values of correlation coefficients (R^2) obtained from Freundlich plots indicate that this model fit the adsorption of metal ions on geopolymer, but they are less than those obtained for Langmuir model, which indicates that

Table 4
Freundlich isotherm parameters for Pb(II) at different temperatures and pH.

| T (°C) | pH=3 | | | pH=4 | | | pH=5 | | |
|--------|----------------|----------------|------|----------------|----------------|------|----------------|----------------|------|
| | R ² | K _F | n | R ² | K _F | n | R ² | K _F | n |
| 25 | 0.9791 | 3.19 | 1.98 | 0.9715 | 4.47 | 1.37 | 0.9350 | 11.73 | 1.64 |
| 35 | 0.9889 | 3.91 | 2.02 | 0.9804 | 5.54 | 1.37 | 0.9640 | 13.39 | 1.55 |
| 45 | 0.9410 | 7.20 | 2.53 | 0.9869 | 6.79 | 1.40 | 0.9538 | 17.62 | 1.47 |

homogenous adsorption is better to describe the process compared to heterogeneous adsorption. Results also indicate that Langmuir model is more applicable than the Freundlich model to describe the adsorption of Pb(II) on geopolymer. Cetin and Pehlivan [19] found similar results for Zn (II) and Ni(II) adsorption on the fly ash. Naseem and Tahir [22] found that the adsorption pattern of lead on bentonite followed the Langmuir isotherm. Li et al. [2], found that the adsorption isotherm of dye by geopolymers can be fitted by Langmuir and Freundlich models.

Table 4 illustrates the values of R^2 , K_f and n at different temperatures and pH value. The value of n ranged from 1.64 to 1.47 in the temperature range from 25 to 45 °C at pH value of 5. The magnitude of constant n is an indicator of linearity of adsorption. The deviation of n from unity indicates a nonlinear adsorption that takes place on the heterogeneous surfaces [22]. According to Tryball [36] n values between 1 and 10 indicate effective adsorption. Since n values for Freundlich isotherm locates between 1 and 10, so it can be concluded that the adsorption process is favorable.

K_f parameter is a temperature dependent where its value increases from 11.73 to 17.62 as temperature increases from 25 to 45 at pH value of 5. The large value of K_f indicates that adsorbent has a high adsorption affinity towards Pb(II) ion [25].

3.5. Thermodynamics of lead adsorption on geopolymer

Thermodynamics of Pb(II) adsorption on geopolymer were investigated at different pH values and different temperatures in the concentrations range 10–140 mg/L. Uptake capacity (q) is calculated according to Eq. (4), then Eq. (8) was used to determine energy parameters, where ($\ln K_d$) was plotted against ($1/T$), which results in a straight line and the values of enthalpy (ΔH^*) and entropy (ΔS^*) are obtained from the slope and intercept. ΔG^* is calculated according to Eq. (9) as illustrated in Table 5.

The positive values of ΔH^* and ΔS^* and the decrease in the value of ΔG^* with the increase of temperature show that the adsorption process is an endothermic process and more favorable at higher temperatures [37]. The endothermicity can be explained by the fact that the metals ions are well solvated [37] and there is strong interaction between adsorbate and adsorbent [22]. In order for metal ions to be adsorbed, they have to lose part of their hydration heat. This dehydration process of the metal ions requires energy. Endothermic nature of the system becomes dominant as the energy of dehydration supersedes the energy of the ions required to be attached on the surface. Energy needed to bond Pb(II) ions to geopolymer matrix exceed the energy of dehydration of Pb(II) ions [25,35,37].

Table 5
Thermodynamic parameter of lead adsorption on geopolymer.

| pH | T (K) | | | R ² | ΔH^* , (kJ/mol) | ΔS^* , (J/mol.K) |
|-----------------------|--------|--------|--------|----------------|-------------------------|--------------------------|
| | 298 | 308 | 318 | | | |
| ΔG^* (kJ/mol) | | | | | | |
| 3 | -14.50 | -15.42 | -16.35 | 1 | 12.98 | 92.23 |
| 4 | -18.19 | -19.46 | -20.73 | 0.9773 | 19.60 | 126.84 |
| 5 | -19.71 | -21.61 | -23.51 | 0.9856 | 36.83 | 189.73 |

The positive value of ΔH° indicates that the entropy of the system increases after adsorption process which also supports the explanation the endothermicity process of the adsorption. When adsorption on geopolimer occurs, the hydrated water molecules are separated from the metal ion before they attach to geopolimer surface or penetrate into its matrix, this will increase the disorder of the heterogeneous system and thus increases its entropy [37].

4. Conclusions

Fly ash-based geopolimer has been successfully synthesized by alkali-activation. The product was highly amorphous structure as revealed by XRD analysis. It was found that the produced geopolimer exhibits higher removal efficiency of Pb(II) when compared to fly ash itself. In addition to examining the adsorption capacity of geopolimer and raw fly ash for Pb removal, the present work also investigates the possible parameters that could affect adsorption process where the optimum conditions are achieved. Also thermodynamic parameters of Pb adsorption on geopolimer are studied and the applicability of two different models is examined.

The removal efficiency increases with increasing geopolimer dosage, contact time, temperature, and the decrease of Pb(II) initial concentration. The optimum removal efficiency was obtained at pH 5. The equilibrium for lead metal ions on the surface of geopolimer occurs quickly and a curing time of 120 min was enough to achieve maximum uptake level Langmuir Model was found to be the best in description of adsorption isotherm indicating the homogeneity of adsorption. The capacity adsorption of Pb(II) is strongly influenced by temperature increasing with the increase of temperature. Furthermore, the positive value of enthalpy (ΔH°) indicates that the adsorption process is endothermic in nature.

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