Modification of fly ash using acids and alkali by hydrothermal method and its application as adsorbents material for phosphate adsorption in aquatic system

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Abstract. In this research, fly ash was modified with acids, such as HCl, H2SO4 and mixture of both and alkali with hydrothermal method. XRF analysis showed a decrease of CaO and Fe2O3 contents in HMFA, SMFA and HSMFA while AMFAWH has higher CaO content and produced the new zeolite phase (hydroxy-sodalite) in $\theta = 24.232^\circ$ from XRD test. FTIR analysis showed that the fly ash gave absorption band of O-H group, H-O-H bend group, and Si-O stretching group. SEM images showed that acid-modified fly ash indicated a deposition of gehlenite crystals while AMFAWH showed flat rectangular shaped small particle known as hydroxy-sodalite. The BET method analysis indicated that all adsorbents were classified as mesopores. The experimental data showed that adsorption efficiency and capacity of fly ash was improved significantly after modification. The unmodified fly ash (UFA) has the highest phosphate adsorption efficiency and capacity in 0.16 g was 60.07 % and 0.485 mg P-PO4/g while modified fly ash (HSMFA) was 85.62 % and 0.705 mg P-PO4/g. The optimum contact time were obtained at 240 min for UFA, HMFA, SMFA and 480 min for HSMFA and AMFAWH. The optimum of pH were obtained at pH 5 and pH 7 for the others. The fifth adsorbents follow the Freundlich isotherm and pseudo-second-order kinetic model in phosphate adsorption.

Keywords: Phosphate, fly ash, acid activation, hydrothermal, adsorption

1. Introduction

Fly ash is a by-products from burning coal in electric power generating plants [1]. In 2008, the total coal produced in Indonesia reached 215 million tons and produced fly ash with large quantities [2]. To solve this problem, a utilization of fly ash that can prevent the environmental pollution is needed. In recent years, fly ash has become a concern of researchers for its use as adsorbents in phosphate adsorption [3].

The unmodified adsorbent has more pores that closed on the surface of adsorbent [4]. To open these closed pores, a modification on adsorbents such as acid-modified fly ash is required, which can dissolve the impurities minerals in the fly ash so the fly ash pores become wider due to the ability to replace the exchanged cation (alkali or soil alkali) in the fly ash structure with ion H+ [5]. Fly ash which has high silica and alumina content, can also be used as an ideal precursor for synthesis of zeolites. Conversion of fly ash into zeolite can be done through an alkali reaction with hydrothermal method [6]. The aim of this research was to examine the effectiveness of acid-modified fly ash and alkali-modified fly ash with hydrothermal method as the adsorbent for phosphate adsorption from aquatic system.
2. Materials and Method

2.1. Materials
Fly ashes were obtained from PT Smart Tbk in Marunda, Indonesia. Fly ashes were washed using DI-water repeatedly and dried at 120 °C for 6 h. They were grounded and passed through a 160 mesh-sized sieve. The reagents used in this research were HCl (37 %), sulfuric acid (96 %), NaOH, and KH₂PO₄, potassium antimony tartrate, ammonium heptamolybdate tetrahydrate and ascorbic acid. All chemical reagents were of analytical grade and obtained from Merck.

2.2. Preparation of acid-modified fly ash adsorbent
Three types of acid solution used were HCl (2 mol/L), H₂SO₄ (2 mol/L) and H₂SO₄-HCl mixture (1 mol/L H₂SO₄ + 1 mol/L HCl). Twenty g of dried coal fly ash was added to 100 mL of acid solution and mixed for 30 min under ultrasonication. The mixtures were then filtered and washed with DI-water until neutral pH. The solid residue was dried at 120 °C for 6 h. After that, the acid-modified fly ash was grounded and sieved with 160 mesh sieve then stored for further test [7].

2.3. Preparation of alkali-modified fly ash with hydrothermal method
Alkaline solution used was 3.5 M NaOH. Twenty g of dried coal fly ash was mixed with 160 mL of 3.5 M NaOH solution in Teflon autoclave and heated at 100 °C in an oven for 24 h. After that, the solid phase was filtered and washed with DI-water until the filtrate pH reached 10. Then, it was dried in an oven at 55 °C for 24 h and stored for further test [6].

2.4. Characterization
Fly ash before and after modified were characterized using XRF, XRD, FTIR, SEM and SSA instrument.

2.5. Study of phosphate adsorption
One thousand mg/L stock phosphate solution was made by dissolving 2.1993 g of KH₂PO₄ in 500 mL of DI-water. Phosphate adsorption was carried out by mixing the adsorbents with phosphate solution in Erlenmeyer flask and stirred using magnetic stirrer. Then, the solution was filtered with Whatman 42 and the filtrate was analyzed by an UV-vis spectrophotometer with molybdenum blue method.

2.5.1. The effect of initial phosphate concentration
The phosphate concentration used for the effect of phosphate concentration were 4 ppm, 6 ppm, 8 ppm, 10 ppm and 12 ppm. The optimum concentration of phosphate solution that obtained will be used for the next experiments.

2.5.2. The effect of pH
The variation of pH in adsorbate solution that used were 3, 5, 7, 10 and 12. It can be controlled by 0.1 M HCl and 0.1 M NaOH. The optimum pH that obtained will be used for the next experiments.

2.5.3. The effect of contact time
The adsorbate solution mixed with adsorbents was stirred using magnetic stirrer for 0.5, 1, 2, 4 and 8 h. The optimum contact time that obtained will be used for the next experiments.

2.5.4. The effect of adsorbent mass
The variation of the adsorbent mass that used were 0.01 to 0.16 g.

3. Results and Discussion

3.1. Characterization of fly ash
The chemical component of fly ash can be seen from XRF characterization in table 1. The content of CaO in acid-modified fly ash (HCl, H₂SO₄ and a mixture of both) is lower than unmodified fly ash. It showed that calcium reacted with acid solutions produce salts that dissolved with water and mostly
removed by filtration process while alkali-modified fly ash with hydrothermal method has a high CaO content due many calcium formed by geopolymerization process [8, 9]. Compared with unmodified fly ash, the content of Fe₂O₃ in acid-modified fly ash is decreased due H⁺ replaces the cation from the fly ash particle of structure lead the dissolution of the metals [10] while alkali-modified fly ash with hydrothermal method has a higher Fe₂O₃ content due the most of amorphous aluminosilicate material has dissolved during geopolymerization reaction [11]. The content of SiO₂ in alkali-modified fly ash with hydrothermal method was lower than unmodified fly ash due to the establishment of new products with different microstructures by exchanging some SiO₂ species with AlO₃ lead to a change in the chemical environment of Si-O bond [12] while acid-modified fly ash has a higher SiO₂ content due to the dissolution of metal oxides and silicon include an element that resistant to acid attack [13].

The diffractograms of the fly ash are shown in figure 1. It indicates the presence of quartz (SiO₂), berlinite (AlPO₄), gehlenite (Ca₂Al(AlSiO₇)) and almandine (Fe₃Al₂(SiO₄)₃) in the fly ash. After modified fly ash with acids (HCl, H₂SO₄ and mixture of both), it shows an increase of the minerals in the sample due to the dissolved minor minerals constituents during acid treatment and quartz minerals becomes more intense [14] while AMFAWH has a lower of quartz and higher of gehlenite contents than UFA due to the hydroxide ions attack the silica forming a gel. The product is calcium silicate hydrate if the gel reacts with calcium ions [15]. In addition, AMFAWH produces the new zeolite phase (hydroxy-sodalite) in 2θ=13.913°, 24.232°, 32.778°, 34.605° and 42.739°.

Table 1. The chemical component of the unmodified fly ash (UFA), HCl modified fly ash (HMFA), H₂SO₄ modified fly ash (SMFA), HCl-H₂SO₄ modified fly ash (HSMFA) and alkali modified fly ash with hydrothermal method (AMFAWH).

| Composition | UFA (%) | HMFA (%) | SMFA (%) | HSMFA (%) | AMFAWH (%) |
|-------------|---------|----------|----------|-----------|------------|
| Al₂O₃       | 16.64   | 16.54    | 16.20    | 16.26     | 12.49      |
| SiO₂        | 48.46   | 61.45    | 65.03    | 60.43     | 30.51      |
| CaO         | 12.10   | 3.25     | 2.57     | 3.52      | 16.77      |
| Fe₂O₃       | 14.80   | 13.10    | 11.00    | 13.68     | 32.52      |

Figure 1. XRD characterization of UFA, HMFA, SMFA, HSMFA and AMFAWH.
FTIR spectra of UFA, HMFA, SMFA, HSMFA and AMFAWH are shown in Figure 2. The broad absorption band of 3650–3200 cm\(^{-1}\) with the peak around 3282 cm\(^{-1}\) in UFA shown as the adsorbed water molecular. After modified with acids (HMFA, SMFA, HSMFA) and alkali with hydrothermal method (AMFAWH) it underwent a shift, respectively at 3294 cm\(^{-1}\), 3309 cm\(^{-1}\), 3382 cm\(^{-1}\) and 3370 cm\(^{-1}\) produced new -OH groups that will increase the phosphate adsorption [7]. The bands at 1606 cm\(^{-1}\) in UFA are demonstrated as H-O-H bending vibration. After modified with acids (HMFA, SMFA and HSMFA) and AMFAWH it underwent a shift, respectively at 1609 cm\(^{-1}\), 1624 cm\(^{-1}\), 1635 cm\(^{-1}\) and 1643 cm\(^{-1}\) defining the H-O-H deformation [6]. The bands at 1045 cm\(^{-1}\) in UFA is defined as Si-O stretching [7]. After modified with acids (HMFA, SMFA and HSMFA) it underwent a shift, respectively at 1058 cm\(^{-1}\), 1097 cm\(^{-1}\), 1101 cm\(^{-1}\) indicating that modification with acid can dissolve impurity that stuck in the active sites for adsorption while AMFAWH underwent a shift to lower band and became sharper (1000 cm\(^{-1}\)) indicating new products by alkali attack such as hydroxy-sodalite in the result of XRD previously mentioned [6].

The surface morphology of UFA, HMFA, SMFA, HSMFA and AMFAWH can be seen in Figure 3. UFA (Figure 3a) typically has spherical shapes with different sizes. After modified with HCl (Figure 3b), it shows the presence of a more uniform particle size and forms several holes. It was due to the stable glassy layers destroyed by reaction between HCl with fly ash [16]. On the other hand, modification with H\(_2\)SO\(_4\) (Figure 3c) shows a white layer on the surface which defined that gehlenite crystals were deposited by sulphate anion attack [17]. HSMFA (Figure 3d) have morphologies that similar with modification HCl and H\(_2\)SO\(_4\) while AMFAWH (Figure 3e) shows the presence of rectangular shaped particles known as hydroxy-sodalite [18].

Porous structure of fly ash was analyzed using SSA by BET method and the results can be seen in Table 2. It shows that HMFA, SMFA, HSMFA and AMFAWH have a larger BET surface area and total pore volume than UFA. The pore size distribution of UFA, HMFA, SMFA, HSMFA and AMFAWH are classified as mesopores due to their sizes were ranged 2–50 nm. The results indicate that HMFA, SMFA and HSMFA can dissolve the impurity that stuck in the active sites for adsorption while AMFAWH produce new cavities from cracked the Si-O and Al-O bond tetrahedron structure so the surface area can be increased [8].

Figure 2. FTIR spectra of UFA, HMFA, SMFA, HSMFA and AMFAWH.
Figure 3. SEM images of (a) UFA, (b) HMFA, (c) SMFA, (d) HSMFA and (e) AMFAWH.

| Material   | BET surface area (m² g⁻¹) | Mean pore diameter (nm) | Total pore volume (cm³ g⁻¹) |
|------------|---------------------------|-------------------------|-----------------------------|
| UFA        | 17.348                    | 3.8602                  | 2.488x10⁻²                   |
| HMFA       | 21.773                    | 3.8658                  | 2.725x10⁻²                   |
| SMFA       | 25.661                    | 3.8669                  | 2.997x10⁻²                   |
| HSMFA      | 45.768                    | 3.8726                  | 4.929x10⁻²                   |
| AMFAWH     | 35.041                    | 3.8680                  | 5.258x10⁻²                   |

3.2. Study of phosphate adsorption
Adsorption mechanism that happened in acid-modified fly ash were the ligand exchange between -OH on the surface of fly ash with phosphate (in solution) [19]. Meanwhile, the adsorption mechanism on alkali-modified fly ash with hydrothermal method was the precipitation of calcium phosphate [20].

3.2.1. Effect of initial phosphate concentration. Figure 4 indicates the adsorption efficiency and capacity from the effect of initial phosphate concentration on the adsorbents. UFA has the highest phosphate adsorption efficiency and capacity of 32.01 % and 1.980 mg P/g while HMFA, SMFA, HSMFA and AMFAWH have the highest phosphate adsorption efficiency and capacity, respectively 41.15 %, 48.99 %, 55.52 %, and 3.545 mg P-PO₄/g, 3.030 mg P-PO₄/g, 3.879 mg P-PO₄/g and 3.434 mg P-PO₄/g. It implies that the amount of adsorbed phosphate increases due to all active sites available on each adsorbents are used for the adsorption at a higher concentration [21].

3.2.2. Effect of pH. The effect of pH on phosphate adsorption is presented in figure 5. It was observed that UFA has the maximum phosphate adsorption efficiency and capacity of 36.71 % and 2.389 mg P-PO₄/g occurred at pH 5 while HMFA, SMFA, HSMFA and AMFAWH have the maximum phosphate adsorption efficiency and capacity, respectively 51.59 %, 61.15 %, 79.94 %, 78.34 % and 3.336 mg P-PO₄/g.
P-PO₄/g, 3.954 mg P-PO₄/g, 5.066 mg P-PO₄/g and 5.169 mg P-PO₄/g. The maximum phosphate adsorption occurred at pH 5 and 7 due to both of the pH values are lower than the pKₐ value of H₂PO₄⁻ (7.2) lead to more protons donated than hydroxide groups by the solution phase so the surface of adsorbents becomes positively charged and attracting phosphate species which negatively charged [22].

3.2.3. The effect of contact time. The effect of contact time on phosphate adsorption is presented in figure 6. It was observed that UFA, HMFA and SMFA have the maximum phosphate adsorption efficiency and capacity in 240 min, respectively 51.62 %, 63.14 %, 69.25 % and 3.230 mg P-PO₄/g, 4.005 mg P-PO₄/g and 4.393 mg P-PO₄/g while HSMFA and AMFAWH have the maximum phosphate adsorption efficiency and capacity in 480 min, respectively 88.26 %, 82.15 % and 5.599 mg P/g, 5.211 mg P-PO₄/g. The first step of phosphate adsorption was in 0–120 min, the availability of surface area and pore sites of each adsorbent were still abundant so the rate of adsorption increased. In the next step, surface area and pores sites of the fly ash became saturated with phosphates lead to the decrease of rate of adsorption [22].

Figure 4. Adsorption (a) efficiency and (b) capacity from the effect of initial phosphate concentration on UFA, HMFA, SMFA, HSMFA and AMFAWH.

Figure 5. Adsorption (a) efficiency and (b) capacity from the effect of pH on UFA, HMFA, SMFA, HSMFA and AMFAWH.
3.2.4. The effect of adsorbent mass. The effect of adsorbent mass on phosphate adsorption is shown in figure 7. UFA, HMFA, SMFA, AMFAWH and HSMFA have the maximum phosphate adsorption efficiency in 0.16 g, respectively 60.07 %, 73.58 %, 79.60 %, 82.27 % and 85.62 % with adsorption capacity, respectively of 0.485 mg P-PO₄/g, 0.606 mg P-PO₄/g, 0.655 mg P-PO₄/g, 0.677 mg P-PO₄/g and 0.705 mg P-PO₄/g. The availability of adsorption sites for phosphate ions will be more in the higher adsorbent masses. However, the graph also shows that the adsorption capacity reduces with the increase in the mass of adsorbents because the active sites of the adsorbent is more unsaturated during the phosphate adsorption process [23].

3.2.5. Isotherm adsorption. From the varied initial phosphate concentrations, isotherm for this research can be estimated from plotting the curves as comparison among Langmuir and Freundlich. The results are summarized in table 3. The values of R² that obtained from Freundlich model was closer to 1 than Langmuir model. In addition, the values of K_f was higher than q_m also. It showed that phosphate adsorption using the fifth adsorbents followed the Freundlich isotherm model which were multilayer adsorption.

Figure 6. Adsorption (a) efficiency and (b) capacity from the effect of contact time on UFA, HMFA, SMFA, HSMFA and AMFAWH.

Figure 7. Adsorption (a) efficiency and (b) capacity from the effect of adsorbent mass on UFA, HMFA, SMFA, HSMFA and AMFAWH.
Table 3. Phosphate adsorption isotherm parameter with fly ash as adsorbent.

| Adsorbent | KL (mg P/g) | qm (mg P/g) | R² | KF (mg P/g) | n | R² |
|-----------|-------------|-------------|----|-------------|---|----|
| UFA       | -0.0749     | -1.3037     | 0.956 | 0.0524 | 0.5857 | 0.972 |
| HMFA      | -0.0923     | -1.4973     | 0.934 | 0.0671 | 0.5356 | 0.983 |
| SMFA      | -0.0767     | -3.3056     | 0.988 | 0.1817 | 0.6567 | 0.998 |
| HSMFA     | -0.1376     | -2.3906     | 0.985 | 0.2111 | 0.5233 | 0.996 |
| AMFAWH    | -0.1115     | -2.2307     | 0.966 | 0.1524 | 0.5525 | 0.987 |

Table 4. The kinetic model parameters for phosphate adsorption on fly ash adsorbent.

| Adsorbents | qe,exp (mg/g) | k1 (min⁻¹) | qe,cal (mg/g) | R² | k2 (g/mg.min) | qe,cal (mg/g) | R² |
|------------|---------------|-------------|----------------|----|---------------|----------------|----|
| UFA        | 3.230         | 0.0006909   | 1.363          | 0.4889 | 0.0199365   | 3.321          | 0.9982 |
| HMFA       | 4.005         | 0.0006909   | 1.288          | 0.5602 | 0.0206685   | 4.050          | 0.9991 |
| SMFA       | 4.393         | 0.0006909   | 1.301          | 0.5641 | 0.0175417   | 4.460          | 0.9989 |
| HSMFA      | 5.599         | 0.0009212   | 1.454          | 0.7777 | 0.0064237   | 5.907          | 0.9986 |
| AMFAWH     | 5.211         | 0.0009212   | 1.408          | 0.7240 | 0.0081536   | 5.470          | 0.9993 |

3.2.6. Adsorption kinetics. The kinetic model parameters obtained by fitting the experimental data are summarized in table 4. The values of qe,cal that obtained from pseudo-second-order kinetic model is closer to the experimental results (qe,exp) than pseudo-first-order kinetic model. It showed that adsorption process that occurred was chemisorption involving the precipitation and ligand exchange.

4. Conclusion
Acid-modified fly ash (HMFA, SMFA and HSMFA) and alkali-modified fly ash with hydrothermal method (AMFAWH) can used as adsorbents for the effective phosphate adsorption. The experimental data shows that HMFA, SMFA, HSMFA and AMFAWH have the highest phosphate adsorption efficiency and capacity in 0.16 g, respectively of 73.58 %, 79.60 %, 85.62 %, 82.27 % and 0.606 mg P-PO4/g, 0.655 mg P-PO4/g, 0.705 mg P-PO4/g and 0.677 mg P-PO4/g while the unmodified fly ash (UFA) has the highest phosphate adsorption efficiency and capacity of 60.07 % and 0.485 mg P-PO4/g. The adsorption efficiency was strongly depended on pH. The optimum condition from the effect of pH were obtained at pH 5 for UFA and pH 7 for HMFA, SMFA, HSMFA and AMFAWH. The contact time represents the time needed for the adsorption process to reach the equilibrium. The optimum contact time for phosphate adsorption were 240 min for UFA, HMFA, SMFA and 480 min for HSMFA and AMFAWH. The fifth adsorbents followed the Freundlich isotherm and pseudo-second-order kinetic model in phosphate adsorption.

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