Low-temperature alkali-modified fly ash as an effective adsorbent for removal of ammonia nitrogen, phosphorus and COD from the wastewater

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Abstract. In this study, low-temperature alkali-modified fly ash and polymeric aluminum chloride (PAC) for the removal of total phosphorus, COD and ammonia nitrogen, from wastewater was systematically investigated. The removal rate of ammonia nitrogen was 81.10\%, and the removal rates of phosphorus and COD were 90.21\% and 55.48\%, respectively. When a dosage of the alkali-modified fly ash was 5g/L, the amount of PAC was 50mg/L, and the mixing time was 39min. In comparison with raw fly ash, the removal rate of ammonia nitrogen is 80.16\% higher than that of the original fly ash, and the removal rate of total phosphorus is 35.48\% higher. Fly ash with improved surface can be used as an alternative adsorbent to flocculate and precipitate in cooperation with polymeric aluminum chloride, which can be applied to the treatment of total phosphorus, COD and ammonia nitrogen in the sewage. This study provides a theoretical basis for the coagulation adsorption method and realizes the utilization of fly ash.

1. Introduction
At present, with the rapid development of modern industry, the surface water is seriously polluted, which has posed a great threat to the river ecological lake system\cite{1}. Urban domestic sewage, agricultural sewage and various industrial wastewater contained a large number of heavy metals, organic matter, ammonia nitrogen, phosphorus, suspended solids, etc., which have the characteristics of complex species, wide influence and large quantity\cite{2, 3}. A large amount of sewage is directly or indirectly discharged into rivers and lakes. Nitrogen, phosphorus and other nutrient elements are likely to cause the outbreak of algae in the water body, resulting in serious eutrophication of the water body and the deterioration of the water environmental quality \cite{4-6}. Therefore, it is difficult for urban inland rivers to meet the requirements of category IV water quality indicators in the Environmental Quality Standards for Surface Water. The development of efficient and energy-saving adsorption materials is the key to the removal of ammonia, total phosphorus, heavy metals and COD in wastewater \cite{7}.

The main methods currently used for wastewater treatment are physical method, biological/ecological method and chemical method \cite{8}. Among them, the chemical adsorption method is widely used in river water treatment, with the advantages of short repair cycle, low operation cost and strong repair ability\cite{9,10}. Flocculation and precipitation can remove heavy metals, nitrogen, phosphorus and COD from wastewater, and improve the water clarity \cite{2, 3}. Therefore, flocculation
and sedimentation is one of important method to treat highly polluted rivers [11]. Common coagulants include polyaluminum chloride (PAC), ferric chloride and polyacrylamide. Among them, PAC and polyacrylamide are less corrosive to the equipment and highly adaptable to temperature and pH, but their sedimentation performance is not good [12]. Thus, using flocculant alone has the problems of poor coagulation effect and low treatment efficiency [11].

Coal-fired power generation is the leading power source in China, and the annual coal ash emission is nearly 100 million tons [13, 14]. Fly ash with large specific surface area, loose and porous surface and active groups, has chemical and physical adsorption activities. Fly ash can absorb and precipitate ammonia nitrogen, phosphorus, heavy metal ions, and dyes in wastewater. Therefore, in last several years, Coal burning bottom ash has been widely used in wastewater purification and environmental pollution control [3, 15]. However, the surface activity of the raw fly ash is relatively low and the adsorption capacity is limited. A lot of research were focused on the improvement of coal fly ash. Through modification, the specific surface area of coal fly ash is increased, and the surface activated aluminum and silicon are released, so that fly ash shows better performance in wastewater treatment [3, 16]. The heavy metal removal is significantly improved by low-temperature alkali modification of fly ash. However, the direct application of improved coal fly ash to remove COD in sewage has many problems such a large number of as suspended particles and difficulty in sedimentation.

In this study, fly ash before and after modification mixing with coagulant was used to treat polluted river water [17]. The content of total phosphorus, ammonia nitrogen and COD in the sewage before and after treatment was determined by chemical methods, and the fly ash before and after alkali modification was represented by BET, XRD, XRF and SEM. This study compares the advantages of combining alkali-modified fly ash (AFA) with PAC in water treatment, provides a theoretical basis for exploring the modification mechanism of fly ash and flocculation precipitation mechanism, and provides a scientific basis for industrial waste utilization.

2. Materials and methods

2.1. Materials and reagents
Coal fly ash was gathered from the electrostatic precipitator of Datong Second Power. Sodium hydroxide is analytical pure, purchased from Sinopharm Group Chemical Reagent Co. Wastewater was obtained from the polluted river water in Changping District, Beijing. The measured concentrations of ammonia nitrogen, COD and total phosphorus in the raw sewage were 2.71, 0.419 and 42 mg/L, respectively.

2.2. Alkali modification of fly ash
The fly ash and sodium hydroxide were thoroughly mixed to obtain mixed materials (the ratio of fly ash to solid alkali is 10:1). The mixture was calcined in a rotary furnace at a temperature of 200°C, and the reaction time was 2h. After cooling, the materials were ground and reserved, and lower temperature alkali improved coal fly ash was obtained.

2.3. Adsorption experiments
1000mL of wastewater was added into the beaker, and adsorbent (low-temperature alkali modified fly ash) was added, the commixture was quickly stirred for 25 min, with a stirring rate of 350 r/min. Then PAC flocculant was added, and the commixture was rapidly stirred for 4 min at a speed of 300-400 r/min., then slowly stirred for 5 min at 50-60 r/min. After standing for 30 min, the content of COD, total phosphorus and ammonia nitrogen of the supernatant was detected [18].

The determination method of ammonia nitrogen, COD and total phosphorus in aqueous solutions as follows: the way for the measurement of total phosphorus refer to the ammonium molybdate spectrophotometric method for the measurement of total phosphorus in water quality (GB11893-89), the detection wavelength was at 700 nm. Determination of ammonia nitrogen refer to Na's reagent spectrophotometric method for determination of ammonia nitrogen in water quality (HJ535-2009), the
detection wavelength was at 420nm. For the determination of COD, please refer to HJ/T399-2007 for the determination of chemical oxygen demand in water by rapid digestion spectrophotometry [11]. The removal rate is calculated as follows:

$$\text{Removal rate} = \frac{C_0 - C_e}{C_0} \times 100\%$$

Where, $C_0$ is the initial concentration of the pollutant, and $C_e$ is the residual concentration of the pollutant after treatment.

2.4. Characterization

X-ray fluorescence spectroscopy (XRF) was used to analyze the elemental composition of Fe, Al and Si in the fly ash before and after improvement. Barrett-Emmett-Teller (BET) method and Langmuir method was used to measured the specific surface area. The mineral phase composition of the sample was analyzed by X-ray diffractometer, working conditions: Cu target, Kα radiation source, tube voltage 40 kV, tube current 40 mA, scan range 0.5 to 10°, scan rate 1°/min.

3. Result and discussion

3.1. Characterization of fly ash before and after modification

3.1.1. Composition of elements. The elemental component of the fly ash before and after modification by alkali is shown in the Table.1. It can be seen that the quality of SiO$_2$, Al$_2$O$_3$ and CaO in the modified fly ash is improved. This may be due to the fact that SiO$_2$ and Al$_2$O$_3$ on the surface of fly ash can react chemically with sodium hydroxide.

| | Al$_2$O$_3$ | SiO$_2$ | Fe$_2$O$_3$ | CaO |
|---|---|---|---|---|
| Fly ash | 31.2 | 36.6 | 2.98 | 2.17 |
| AFA | 34.5 | 42.0 | 2.41 | 2.34 |
| Change the amount | 3.3 | 5.4 | -0.57 | 0.17 |

3.1.2. Surface characteristics and micro morphology. The specific surface area of raw ash was 1.58m$^2$/g. After modification by alkali, the specific surface area was 23.6m$^2$/g, increasing by 13.9 times. The SEM characterization results show that the morphology of the raw ash and low-temperature alkali-modified fly ash as greatly differed. The morphological structure of raw ash was a glass spherical structure with a smooth surface (as show in Figure 1a). After the fly ash undergoes a low-temperature alkali treatment reaction, the originally smooth glass spheres were dispersed into a flaky particle structure (as show in Figure 1b), which resulting larger specific surface area and the significant porous structure.

![Figure 1. SEM images of FA(a), AFA(b).](image-url)
3.1.3. XRD analysis. To determine the crystal composition of the alkali-modified fly ash, XRD characterization of the fly ash at each stage was performed (including: raw ash, alkali modified ash). As shown in Figure 2, the main crystal structure of raw ash is the crystal form of mullite. There are "steamed buns peak" between 10-30°C, which show that there are still many amorphous structures in fly ash. After modification, there are only "steamed bun peaks" in treated fly ash, the crystal peaks no longer existing. The results showed that the mullite structure was destroyed by low temperature alkali treatment and only amorphous silica-aluminum structure existed in the structure.

![Figure 2. XRD patterns of FA, AFA.](image)

3.2. The removal of phosphorus, ammonia nitrogen and COD

3.2.1. Comparison of removal performance. The concentrations of total phosphorus, ammonia nitrogen and COD in the raw sewage were 0.419, 2.71 and 42 mg/L, respectively. The ratio of fly ash to solid alkali is 10:1, and the adding amount of low-temperature alkali modified fly ash is 32 g/L. As shown in Figure 3, the removal rates of total phosphorus, ammonia nitrogen and COD in the raw sewage treated with PAC only were 1.36%, 45.92%, and 13.34% respectively. When the raw sewage was treated with FA, the removal rates of total phosphorus, ammonia nitrogen and COD were 36.36%, 39.03% and 13.34% respectively. As sewage was treated with AFA, the removal rates of total phosphorus, ammonia nitrogen and COD were 88.18%, 69.36% and 6.65%, respectively. The removal rate of COD and total phosphorus is lower when PAC was used alone to treat sewage. Compared with FA, adding alkali modified fly ash can greatly improve the removal rate of phosphorus and ammonia nitrogen, but the removal rate of COD in river water is lower. Therefore, it is difficult for alkali modified fly ash or PAC used only to remove ammonia nitrogen, COD and phosphorus in sewage.

3.2.2. Effect of combination of fly ash and PAC. The adding amount of low-temperature alkali modified fly ash and PAC is 5 g/L and 50 mg/L, respectively and the ratio of fly ash to solid alkali is 10:1, the result is shown in Figure 4. After the flocculation-precipitation treatment of AFA and PAC, the removal rates of total phosphorus, ammonia nitrogen and COD were 90.21%, 81.10% and 55.48% respectively. And the concentrations of total phosphorus, ammonia nitrogen and COD of the effluent could meet the environmental quality standards of type II surface water. Compared with the original fly ash, the removal rate of ammonia nitrogen and total phosphorus increased by 80.16% and 35.48% respectively. It is due to the existence of a large numbers of exchangeable cations (e.g., Al^{3+}, Fe^{3+}, Na^+) on the surface of the alkali-modified fly ash, which has electrostatic attraction and can be ion-exchanged with NH_4^+ in sewage [19-21]. The loss rate of iron in the modification process is small, and it can precipitate with phosphoric acid, which is the result of the simultaneous action of ion exchange and physical adsorption. Hydrolysis of aluminum ions generates mono- and polynuclear polymers, which form large flocs by adsorption bridging to effectively remove COD.

3.2.3. Effect of the dgoe of adsorbent. To explore the influence of the amount of fly ash on the adsorption performance, increase the dgoe of adsorbent to 32g/L. As shown in Figure 5, after low
temperature alkali modified fly ash and PAC flocculation and precipitation, the removal rates of total phosphorus, ammonia nitrogen and COD were 21.90%, 96.71% and 85.20%, respectively. Compared with FA, total phosphorus and ammonia nitrogen increased by 74.62% and 39.49% respectively. As the amount of alkali-modified fly ash increases, the turbidity of water increases, and during the settling process, the repulsive force between the fly ash gradually increases. The adsorption results showed poor results for COD removal, probably due to the alkali-modified fly ash affecting the pH of the water. Therefore, as the amount of alkali-modified fly ash increases, the removal rate of COD decreases. Compared with the addition of alkali-modified fly ash alone, the removal rate of COD increased by 2.29 times with the addition of PAC.

![Figure 3](image1.png)

**Figure 3.** The removal rate of total phosphorus, ammonia nitrogen and COD in sewage, as raw fly ash (FA), alkali modified fly ash (AFA) and PAC were added respectively.

![Figure 4](image2.png)

**Figure 4.** The removal rate of total phosphorus, ammonia nitrogen and COD in sewage with a dosage of 5g/L alkali modified fly ash (AFA) /fly ash (FA) and 50mg/L PAC.

![Figure 5](image3.png)

**Figure 5.** The removal rate of total phosphorus, ammonia nitrogen and COD in sewage with a dosage of 32g/L alkali modified fly ash (AFA) /fly ash (FA) and 50mg/L PAC.

According to the above results, after the fly ash alkali modification, the surface roughness and disorder are increased, and the specific surface area was significantly improved. Therefore, the removal rate of total phosphorus and ammonia nitrogen was also greatly enhanced. The main adsorption method in combination with PAC is ion exchange and chemical precipitation. The poor removal effect of COD may be due to the increase of the repulsive force between the fly ash and the high pH. Of course, the influence of temperature and pH cannot be ignored. The focus of the next step
will be to further study the factors that affect the removal of total phosphorus, ammonia nitrogen and COD in the wastewater with alkali-modified fly ash, and do an in-depth study on the removal mechanism.

4. Conclusion
In this study, low-temperature alkali method was used to modify fly ash, and in combination with PAC, the ammonia nitrogen, phosphorus and COD in sewage were well adsorbed. The structure was characterized by SEM and XRD analysis. When the adding amount of low-temperature alkali modified fly ash and PAC is 5g/L and 50 mg/L, respectively, sewage effluent can meet the environmental quality standards of type II surface water. Therefore, this study prepared a high-performance adsorbent, which can quickly and effectively absorb ammonia nitrogen and phosphorus in sewage, and also provided a theoretical foundation for the combined use of flocculant to purify sewage.

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References
[1] Ibrahim, S., El-Liethy, M. A., Elwakeel, et al. Role of identified bacterial consortium in treatment of Quhafa Wastewater Treatment Plant influent in Fayoum, Egypt[J]. Environ Monit Assess, 2020, 192:161.
[2] Hosseini Asl S M, Javadian H, Khavarpour M, et al. Porous adsorbents derived from coal fly ash as cost-effective and environmentally-friendly sources of aluminosilicate for sequestration of aqueous and gaseous pollutants: A review[J]. Journal of Cleaner Production, 2019, 208: 1131-1147.
[3] Mushtaq F, Zahid M, Bhatti I A, et al. Possible applications of coal fly ash in wastewater treatment[J]. Journal of Environmental Management, 2019, 240: 27-46.
[4] Luo Y, Wu Y, Ma S, et al. An eco-friendly and cleaner process for preparing architectural ceramics from coal fly ash: Pre-activation of coal fly ash by a mechanochemical method[J]. Journal of Cleaner Production, 2019, 214: 419-428.
[5] Can O T, Gengec E, Kobya M. TOC and COD removal from instant coffee and coffee products production wastewater by chemical coagulation assisted electrooxidation[J]. Journal of Water Process Engineering, 2019, 28: 28-35.
[6] Cardoso A M, Horn M B, Ferret L S, et al. Integrated synthesis of zeolites 4A and Na–P1 using coal fly ash for application in the formulation of detergents and swine wastewater treatment[J]. Journal of Hazardous Materials, 2015, 287: 69-77.
[7] Muath Almughamisi, M. S., Khan, Z. A., Alshitari, W., & Elwakeel, K. Z. (2019). Recovery of Chromium(VI) Oxyanions from Aqueous Solution Using Cu(OH)2 and CuO Embedded Chitosan Adsorbents. Journal of Polymers and the Environment. doi:10.1007/s10924-019-01575-z.
[8] Zhang B H, Wu D Y, Wang C, et al. Simultaneous removal of ammonium and phosphate by zeolite synthesized from coal fly ash as influenced by acid treatment[J]. J Environ Sci (China), 2007, 19(5): 540-545.
[9] Jiang, C., Wang, X., Qin, et al. Adsorption mechanism of ammonia-Nitrogen wastewater in rare-Earth with modified fly ash[J]. Nonferrous metals(extractive metallurgy), 2017, (10): 71-74.
[10] Temel, Farabi, & Kutluay, S. (2020). Investigation of High-Performance Adsorption for Benzene and Toluene Vapors by Calix[4]arene based Organosilica (CBOS). New Journal of Chemistry. doi:10.1039/d0nj02081h
[11] Jiang, C., Wang, X., Qin, et al., Construction of magnetic lignin-based adsorbent and its
adsorption properties for dyes. Journal of Hazardous Materials. [J]. Journal of Hazardous Materials, 2019, 369: 50-61.

[12] Kuang, Yan, Gao, Y., et al. Effect of initial pH on the sludge fermentation performance enhanced by aged refuse at low temperature of 10 ℃. Environmental Science and Pollution Research [J]. Environmental Science and Pollution Research, 2020. https://doi.org/10.1007/s11356-020-09306-x

[13] Soto-Pérez L, Hwang S. Mix design and pollution control potential of pervious concrete with non-compliant waste fly ash [J]. Journal of Environmental Management, 2016, 176: 112-118.

[14] Cardoso A M, Horn M B, Ferret L S, et al. Integrated synthesis of zeolites 4A and Na–P1 using coal fly ash for application in the formulation of detergents and swine wastewater treatment [J]. Journal of Hazardous Materials, 2015, 287: 69-77.

[15] Wang N, Zhao Q, Xu H, et al. Adsorptive treatment of coking wastewater using raw coal fly ash: Adsorption kinetic, thermodynamics and regeneration by Fenton process[J]. Chemosphere, 2018, 210: 624-632.

[16] Li Zheng, Zhang Miao, Xiong Nanni, et al. Performance of nitrogen and phosphorus removal in petrochemical wastewater by fly ash synthetic zeolite [J]. Chemical Engineering (China), 2018, 46(10): 7-10.

[17] A. M. Elgarahy & K. Z. Elwakeel & G. A. Elshoubaky & S. H. Mohammad. Untapped Sepia Shell–Based Composite for the Sorption of Cationic and Anionic Dyes [J]. Water Air Soil Pollut, 2019, 230: 231.

[18] An, C., Yang, S., Huang, G., et al. Removal of sulfonated humic acid from aqueous phase by modified coal fly ash waste: Equilibrium and kinetic adsorption studies[J]. Fuel, 2016, 165, 264-271.

[19] Koshy N, Singh D N. Fly ash zeolites for water treatment applications[J]. Journal of Environmental Chemical Engineering, 2016, 4(2): 1460-1472.

[20] Goscianska J, Ptaszkowska-Koniarz M, Frankowski M, et al. Removal of phosphate from water by lanthanum-modified zeolites obtained from fly ash [J]. Journal of Colloid and Interface Science, 2018, 513: 72-81.

[21] Dogan, M., Temel, F. & Tabakci, M. High-Performance Adsorption of 4-Nitrophenol onto Calix[6]arene-Tethered Silica from Aqueous Solutions [J]. Journal of Inorganic and Organometallic Polymers and Materials (2020). https://doi.org/10.1007/s10904-020-01571-0.