Separation of Aromatic Compounds from Normal Paraffinic Petroleum Mixture Using Geopolymer Adsorbent Based on Metakaolin

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Abstract

Metakaolin-based geopolymers are environmentally sustainable materials that can be synthesized from waste products. In this study, a metakaolin-based geopolymer adsorbent was synthesized, characterized, and evaluated for the removal of aromatic compounds from normal paraffin (C_{10}-C_{13}). The results indicated that modification of the geopolymer adsorbent with activated carbon enhanced its aromatic compound removal efficiency. However, when the activated carbon/metakaolin ratio exceeded 1:12, the removal efficiency declined. Additionally, modification with hydrogen peroxide as a foaming agent resulted in a higher aromatic removal capacity compared to the unmodified geopolymer adsorbent. It was observed that increasing the temperature from 70 to 120 °C enhanced the aromatic removal efficiency by up to 21%. Furthermore, increasing the adsorbent dosage from 0.001 to 0.1 g/L in petroleum samples led to an increase in aromatic compound removal. However, beyond this point, further increases in the adsorbent dosage resulted in a decrease in adsorption capacity.

Introduction

Aromatic hydrocarbons, characterized by the presence of one or more benzene rings, are key raw materials in the petrochemical industry. Despite their high degree of unsaturation, aromatic hydrocarbons exhibit stability and resistance to addition reactions, making them significant environmental pollutants. The U.S. Environmental Protection Agency classifies these compounds as carcinogenic. Additionally, aromatic compounds have an inherently low cetane value, which poses a particular challenge in cold engine startup. High concentrations of polycyclic aromatic hydrocarbons (PAHs) contribute to poor ignition performance in diesel engines, while also exacerbating environmental pollution. Therefore, reducing the content of PAHs in diesel and enhancing its cetane number is of considerable importance for both engine efficiency and environmental sustainability (Liu et al. 2022).

The separation of aromatics from surplus diesel fuel presents a promising approach to advancing the high-end development of the petroleum industry (Li et al. 2023). The separation of aromatic and aliphatic hydrocarbons, a topic of study since the 1960s, remains a crucial process in the chemical industry (Schwarz and Malsch 2005; Hadj-Kali et al. 2017). However, the separation of aromatic hydrocarbons from linear and cyclic aliphatic hydrocarbons is challenging due to the proximity of their boiling points. Furthermore, the similar physical and chemical properties of these compounds make their separation difficult in certain cases. The concentration of aromatic hydrocarbons in the feedstock plays a key role in determining the most suitable separation technology (Ayuso et al. 2020). Conventional methods for separating aromatic and aliphatic hydrocarbon mixtures, such as

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Improved Oil and Gas Recovery

DOI: 10.14800/IOGR.1328

Received October 28, 2024; revised November 20, 2024; accepted December 30, 2024.

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extractive distillation, azeotropic distillation, and liquid–liquid extraction, are well-established (Liu et al. 2018). However, these techniques are often challenging, expensive, and energy-intensive, particularly when separating aromatics from aliphatic mixtures due to their close boiling points and the tendency to form azeotropes (Yao et al. 2019; Feng et al. 2015).

Various methods have been developed for the removal of aromatic compounds from oily mixtures, including Advanced Oxidation Processes (AOPs), adsorption, and biological processes (Yang et al. 2015). Among these, adsorption is widely regarded as an efficient and straightforward method for separation, and it has become a common technique in scientific research. Activated carbon, in its normal or modified form, is frequently employed to remove aromatic organic compounds such as phenol (Lyon-Marion et al. 2018). In recent decades, polymer-based adsorbents have emerged as viable alternatives to activated carbon. Geopolymers, which are inorganic polymeric aluminosilicate materials with an amorphous three-dimensional structure, are derived from industrial by-products such as fly ash, slag, and other waste materials. Due to their excellent chemical and mechanical stability, minimal shrinkage upon formation, high-temperature resistance, and eco-friendly properties, geopolymers have gained significant attention for various applications (Zhang et al. 2014). In separation processes, geopolymers have been utilized as membrane supports, catalyst supports, and adsorbents (Monjezi and Javanbakht 2023; Eshghabadi and Javanbakht 2024). For example, Faghihian and Mousazadeh (2007) investigated the separation of aromatic compounds from normal paraffin (C_{10}-C_{14}) using X13 molecular sieves.

For the removal of cyclic aromatic compounds from water, Kefi et al. (2011) employed titanium nanotubes, achieving removal efficiencies ranging from 90% to 100%. Yao et al. (2015) utilized a Co/Mo $(Co_3)_2$-Layered Double Hydroxide (LDH) adsorbent, which demonstrated up to 94% removal of aromatic substances. Costa et al. (2017) employed a mesoporous Si-MCM-41 molecular sieve for the removal of polycyclic aromatic hydrocarbons, achieving adsorption efficiencies up to 93%. Cyclodextrin-coated silica nanoparticles were used by Topuz and Uyar (2017) for the removal of aromatic compounds. Kumar and Mohan (2018) applied a mixture of 20% glycerin and 80% methanol for the extraction of aromatic compounds from kerosene. In the present study, geopolymer foams were synthesized using metakaolin in an alkaline activation medium with silicate precursors and hydrogen peroxide as a foaming agent. The resulting geopolymer foam was then employed as an adsorbent to remove aromatic compounds from normal paraffin (C_{10}-C_{13}) under various conditions.

Materials and Methods

Materials. The analytical grade of the initial materials was used without further purification. Sodium metasilicate (Na_2SiO_3), potassium hydroxide (KOH), hydrogen peroxide (H_2O_2), sodium hydroxide (NaOH), Nitric acid (HNO_3), and were obtained from Merck company, and metakaolin obtained from Khorasan company. A diesel cut of aromatic (naphthalene and Alkyl benzene) normal paraffin (C_{10}-C_{13}) compounds with 4000 mg/L aromatic concentration was obtained from EORC, Iran.

Characterization. BET analysis for measuring surface area using BET device, Belsorp mini II model, Bel Japan Co. Scanning Electron Microscope (SEM), MIRA III model made in TESCAN for morphological analysis of the samples. A DR-5000 model, Hach UV-Vis spectrometer was used for measurement of sample concentration according to UOP Method 495-00. XRD analysis, Pw1730 model, Philips, was used for studying crystal structure by X-Ray Diffraction Spectrometer Ka Cu ray 1/542 Å wavelength and Nickel Filter.

Fabrication of the Adsorbent. According to **Figure 1**, 15 gr sodium hydroxide was dissolved in 30 mL of distilled water then 60 gr sodium silicate was added to the obtained alkaline solution. After homogenization, 60 gr metakaolin was added to the solution. After mixing, 8 mL hydrogen peroxide (30% v/v solution) was added to the resulted slurry gradually and mixed at 60°C for 2 h. Considering the alkalinity of the combination, Nitric Acid 10 M was used for neutralization. The neutralized substances were filtered and dried in a furnace at 70 °C. To remove impure organic compounds, calcination was done at 500 °C for 24 h (by increasing temperature to

2°C/min). For fabricating adsorbent modified with activated carbon (AC-ADS), 1:12, 1:6, and 1:3 ratio activated carbon were added to the initial suspension containing alkali sodium hydroxide, sodium silicate, and metakaolin. Other stages were like stages of fabrication of base adsorbent (named ADS).

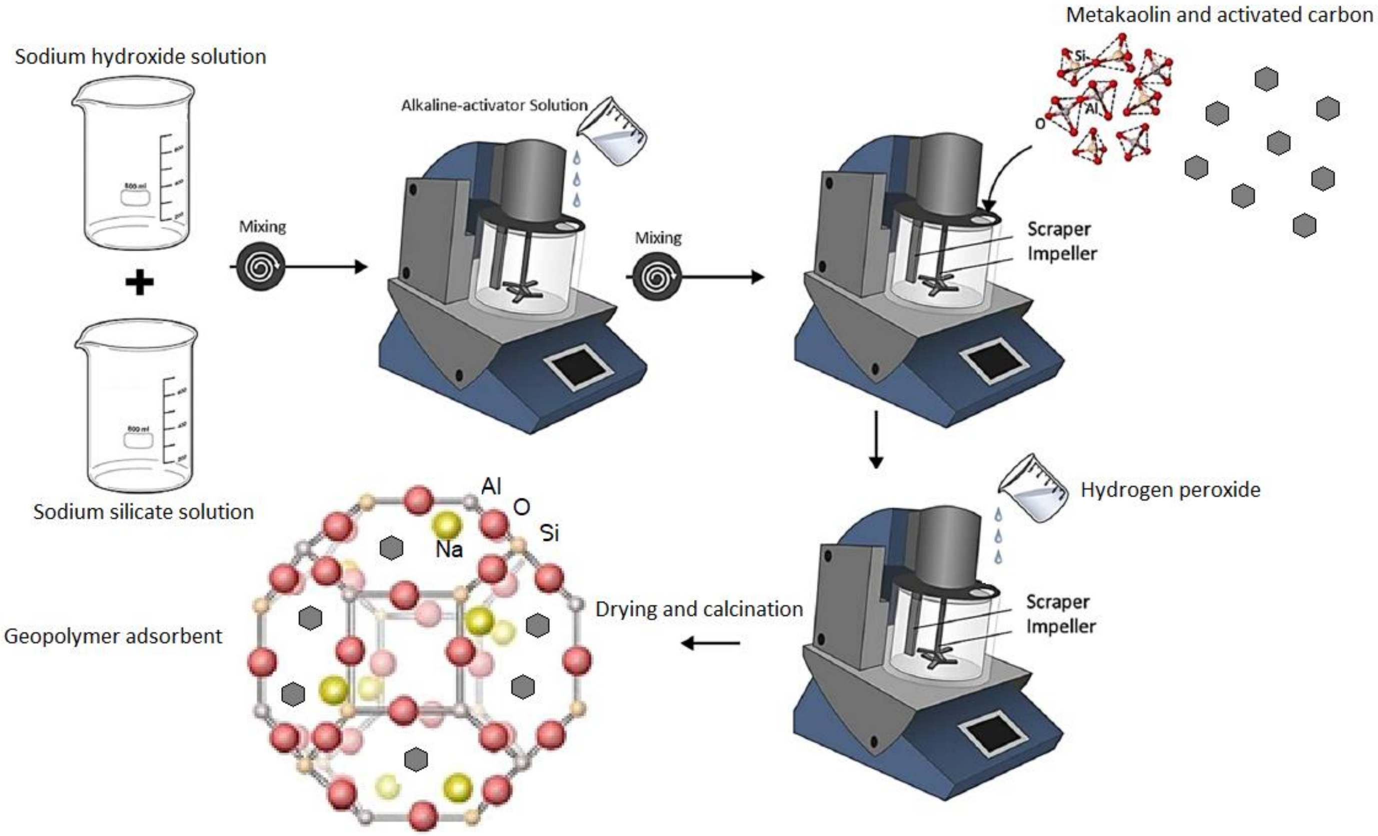


Figure 1—The schematic representation of the adsorbent preparation.

Aromatic Removal Experiments. For aromatic removal experiments, a 1 g/L dose of the adsorbents in a sample of petroleum compounds with initial aromatic concentration of 4000 mg/L was prepared. Then, mixtures containing the petroleum compounds and the adsorbents were shaken at temperatures of 70, 100, and 120 °C and 200 rpm, and sampling was performed at 12 h and their concentration was measured with the UV spectrophotometer. The amount of aromatic removal by the adsorbent was determined using the initial concentration C0 (mg/L), and the final concentration C_f (mg/L) using the following equation,

$$\text{Aromatic removal (\%)} = \frac{C0-Cf}{C0} \times 100\% \quad (1)$$

Results and Discussion

Characterization Results. SEM images of produced adsorbents are shown in **Figure 2**. Based on SEM images, the morphology of the ADS particles is semi-spherical with relatively uniform size distribution but with agglomerating caused by small size of the particles. On the other hand, with modification of the adsorbent with activated carbon, structural changes are observed which is created a non-uniform porous but agglomerated structure in the AC-ADS.

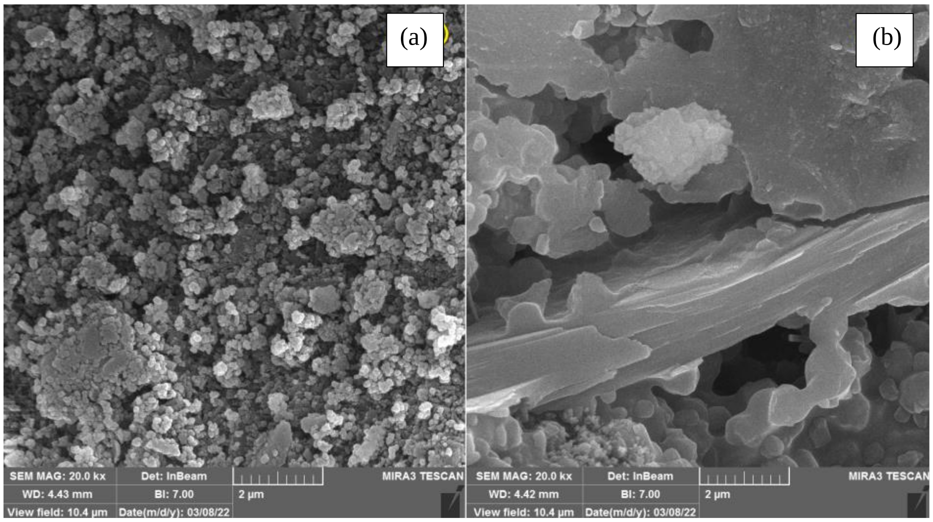


Figure 2—SEM images of the prepared adsorbents of ADS (a) and AC-ADS (b).

Figure 3 shows the XRD spectrum of produced adsorbents of ADS (a) and AC-ADS (b). The XRD pattern illustrates the amorphous characteristics of the prepared geopolymers with some crystalline structures. As observed, no significant changes occurred in the crystalline structure of the initial foam upon modification with activated carbon.

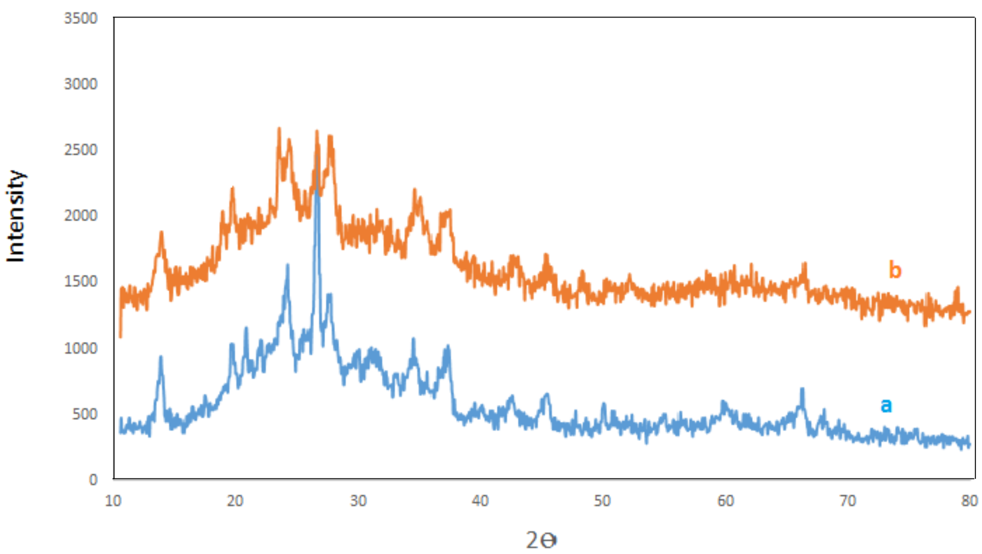
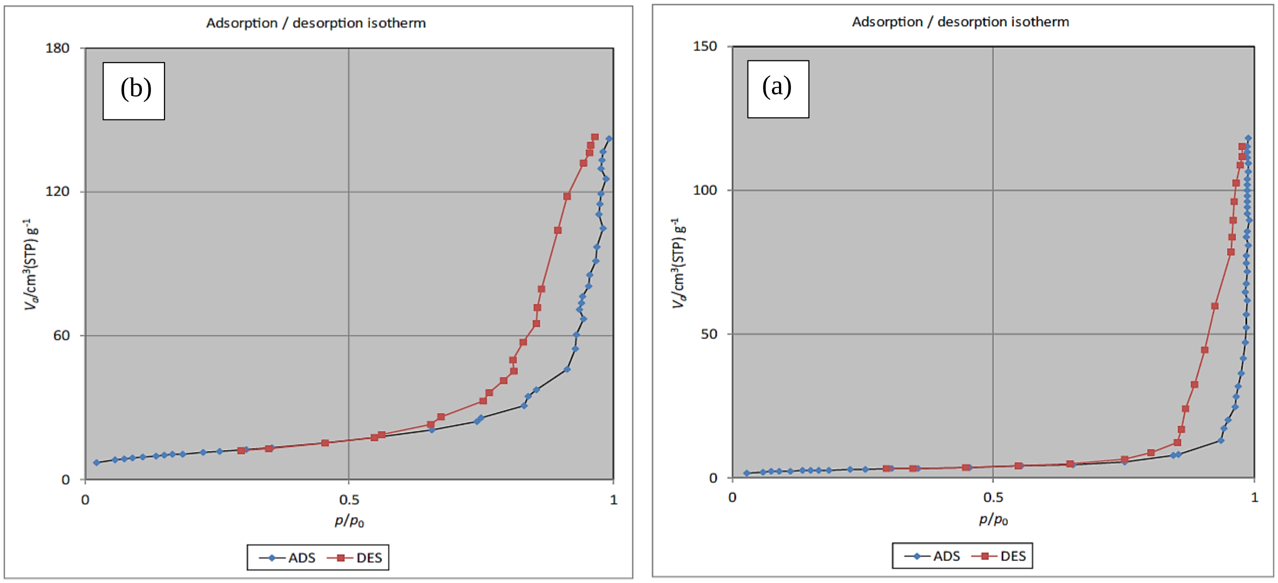


Figure 3—XRD analysis results for ADS (a) and AC-ADS (b).

The nitrogen adsorption-desorption curve is shown in **Figure 4**. The BET results show a typical IV isothermal curve and an H1 hysteresis loop according to the IUPAC classification. The hysteresis loop at high relative pressures reveals the mesoporous structure. According to the BET test data, the specific surface area ($m^2.g^{-1}$) are obtained about 10.14 and 39.33 for ADS and AC-ADS, respectively which represents the surface area increased with the increase of active components in the adsorbent structure. Total volume of the pores ($cm^3.g^{-1}$) of 0.18 and 0.22, and average pore diameter of 72.10 and 22.24, were obtained for ADS and AC-ADS, respectively.



(a)ADS (b)AC- ADS

Figure 4—BET analysis of fabricated adsorbents.

The Results of Aromatic Compounds Removal by Fabricated Adsorbents. Figure 5 shows the effect of temperature on removal of aromatic compounds by ADS and AC-ADS samples, for the petroleum compounds with initial aromatic concentration of 4000 mg/L. As observed, increasing the temperature results in a higher removal percentage of aromatic compounds by the adsorbents. According to the obtained results, the AC-ADS shows a higher ability to aromatic removal in all of temperatures which can be resulted that the modification of the ADS with activated carbon can improve the removal of aromatic compounds.

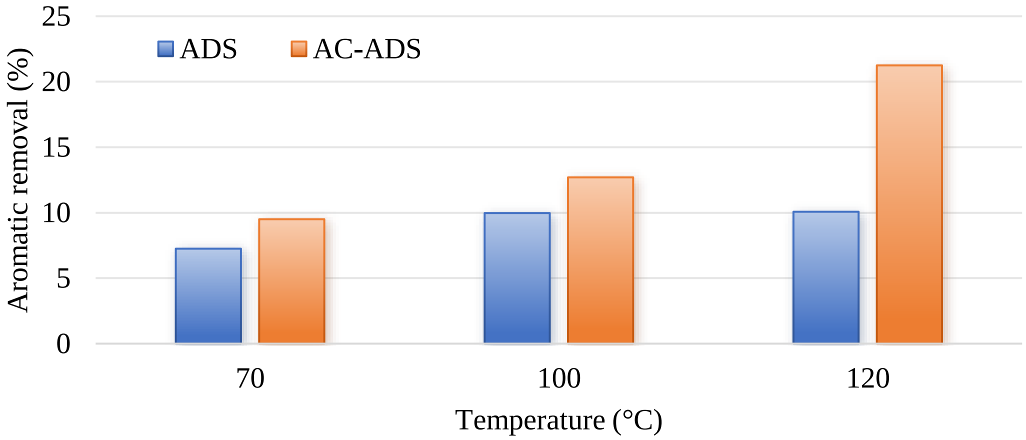


Figure 5—The effect of temperature on the removal of aromatic compounds by the ADS and AC- ADS adsorbents for aromatic concentration of 4000 mg/L and 1 g adsorbent at contact time of 12 h.

Figure 6 shows the effect of hydrogen peroxide as a foaming agent for the adsorbent preparation on removal of aromatic compounds by AC-ADS samples for the petroleum compounds with initial aromatic concentration of 4000 mg/L. The geo-polymerization process causes the formation of porous structures due to the bursting of oxygen bubbles formed by the hydrogen peroxide reaction in the geopolymer substrate (Monjezi and Javanbakht 2023). As it can be observed, the adsorbent modified with foaming agent, illustrates higher capability to aromatic removal which can because to pore creation in the adsorbent structure by hydrogen peroxide that increases the active sites responsible for aromatic adsorption and finally increases the aromatic removal On the other hand, as it can be observed, increasing the temperature increases the aromatic removal with the adsorbent which is consistence with the previous results.

For propose the mechanisms for aromatic compounds adsorption onto the prepared adsorbent, it can be mentioned that aromatic hydrocarbons have high viscosity and strong adsorption capacity (Dang et al. 2019). As observed from the SEM images, the prepared geopolymer consisted of non-flat and uneven surface which helps the mass transfer and uptake of the aromatic molecules onto the adsorbent. Furthermore, electrostatic interaction and n–π interaction because of the presence of metal ions on the surface of the geopolymer such as Al^{3+}, may be the reason for uptake between the geopolymer surface and aromatic molecules.

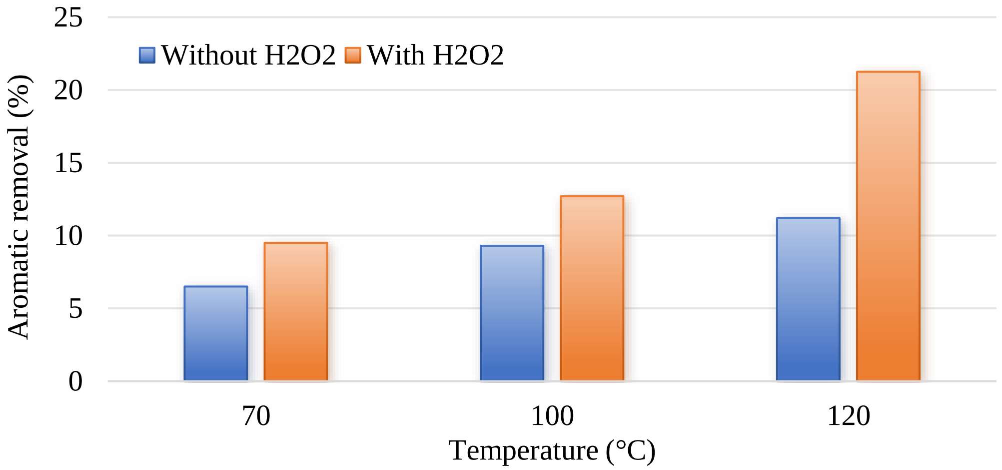


Figure 6—The effect of hydrogen peroxide as a foaming agent for the adsorbent preparation on removal of aromatic compounds by AC-ADS, initial aromatic concentration of 4000 mg/L, 1 g adsorbent at contact time of 12 h and for different temperatures.

As shown in **Figure 7**, by increasing the amount of adsorbent from 0.1 to 1 g, the aromatic removal increased which is due to the availability of more active sites for the adsorption process. Furthermore, with more increase in the adsorbent dosage, the capacity of the adsorption decreases which may be due to increase in diffusion path length resulting from overlapping or aggregation of active sites for adsorption.

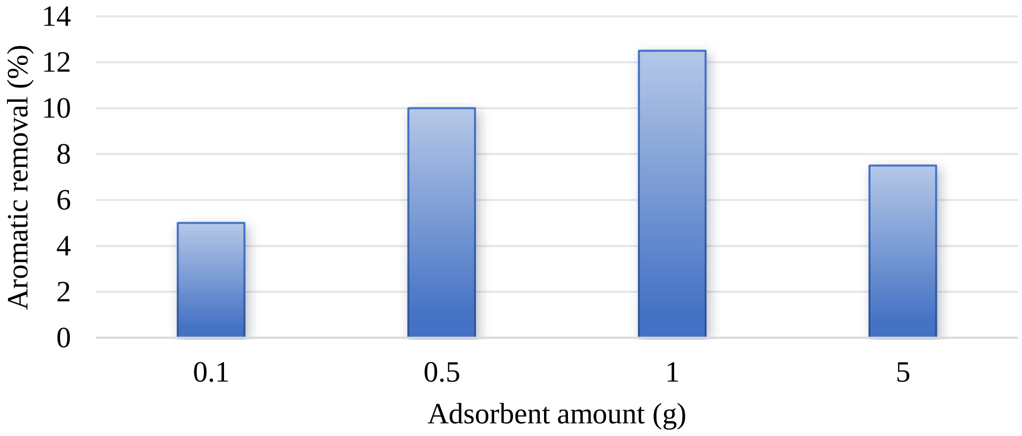


Figure 7—The effect of the adsorbent amount on the removal of aromatic compounds by AC-ADS, initial aromatic concentration of 4000 mg/L.

On the other hand, modification of the geopolymer adsorbent with activated carbon more than 1:12 of ratio activated carbon/metakaolin, reduce the aromatic removal capability (**Figure 8**).

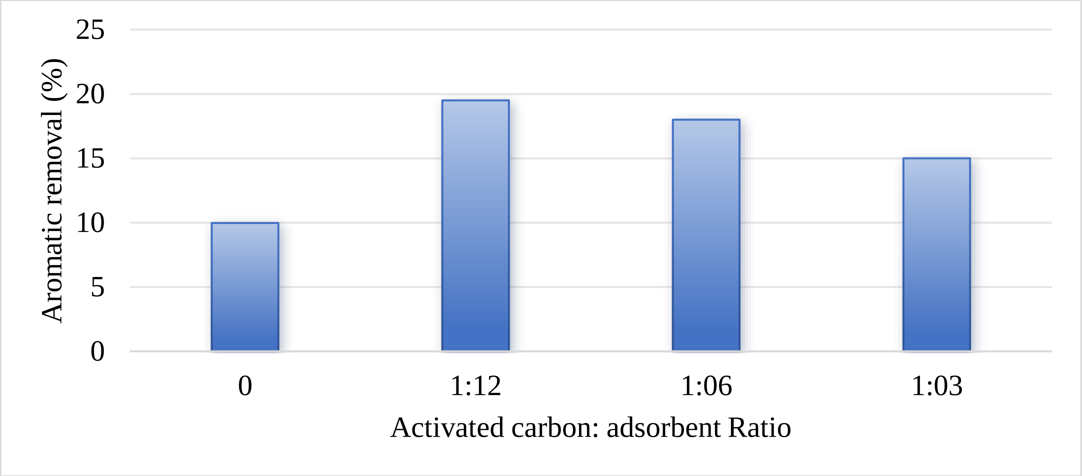


Figure 8—The effect of the activated active content in the AC-ADS on the removal of aromatic compounds, initial aromatic concentration of 4000 mg/L.

Conclusions

A metakaolin-based geopolymer adsorbent was synthesized for the removal of aromatic compounds from normal paraffin. The results indicated that the modification of the adsorbent with activated carbon enhanced the removal of aromatic compounds. However, when the activated carbon/metakaolin ratio exceeded 1:12, the aromatic removal efficiency decreased. In contrast, modification of the geopolymer adsorbent with hydrogen peroxide as a foaming agent significantly improved its aromatic removal capability compared to the unmodified adsorbent. Additionally, increasing the temperature from 70 to 120 °C resulted in an increase in the removal efficiency of aromatic compounds, with up to a 21% improvement. Furthermore, as the adsorbent dosage was increased from 0.001 to 0.1 g/L in petroleum samples, the removal of aromatic compounds enhanced; however, further increases in the adsorbent dosage led to a decrease in the adsorption capacity.

Acknowledgment

Financial support for this work by the ACECR Institute of Higher Education (Isfahan Branch) is gratefully appreciated.

Conflicting Interests

The author(s) declare that they have no conflicting interests.

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