

Kaolin-supported molybdovanado phosphoric acid as green catalyst for fluoride ion removal in water

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Abstract. Using the impregnation approach, molybdovanado phosphoric acid (MVPA) has been immobilized onto kaolin resulting in a green heterogeneous catalyst (MVPA@Kaolin). A comprehensive physicochemical analysis was performed on the catalyst. Because of its uses in fine chemicals and medicines, this hybrid material is meant to be used as a sustainable catalyst. To investigate the catalyst, a variety of physicochemical characterization approaches were used. Through the adsorption of fluoride, the performance of the material was evaluated with temperature, pH, catalyst load, and contact time. The results demonstrated rapid and efficient fluoride removal, with a removal efficiency of more than 85 % in a little contact time. The optimum pH obtained as 1 with fluoride removal efficiency of 84 %, catalyst load 5 g/L (85 %), and temperature 50 °C (85 %). Additionally, composite material regeneration and reusability were investigated. The results aid in the creation of effective and environmentally sustainable fluoride-in water treatments.

1 Introduction

Heteropoly acids (HPA) are essential for synthesis and applications because of their distinct Keggin structure and exceptional redox properties. Their limited surface area and inability to withstand high temperatures limit their application [1-2]. Metals added to the framework may have their acid and redox properties changed for a variety of uses [3]. Vanadium (V) has been shown to produce a large beneficial redox catalysis when added to the Keggin framework using H₂O₂ [2, 3].

The kaolinite possesses high specific surface area, exceptional stability, and environmental friendliness. Effective techniques for enhancing Kaolinite's heavy metal

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adsorption, dye degradation etc. include thermal modification, acid modification, transition metal modification, and organic modification [4, 5]. Water contaminated by fluoride ions is a serious issue that has an impact on animal and human health [6]. Fluoride ions must be present in drinking water at a minimum, however excessive fluoride ion concentrations in water can be harmful to human health, mostly causing skeletal and dental fluorosis [7]. According to Bureau of Indian Standards IS 10500: 2012, the method of checking fluoride (as F) mg/l is IS 3025, as per reference to part 32 of the aforementioned standards. The allowable limit in the absence of a backup source is 1.5 mg/l, while the maximum permitted value is 1 mg/l. The Environment (Protection) Act, 1986, Section 3(3), established the Central Ground Water Authority, whose purpose is to oversee and govern the nation's groundwater resource development and management [8]. In the present work, hybrid Kaolin-supported molybdovanado phosphoric acid has been synthesized for removal of fluoride in water. In contrast to earlier research, this study aims to develop a highly efficient and sustainable catalyst by fusing the special qualities of molybdovanado phosphoric acid and kaolin clay with the concepts of green chemistry. The novel method tackles the problems associated with fluoride ion removal by prioritizing cost-effectiveness, environmental safety, reusability and the possibility of large-scale implementation.

2 Methodology

2.1 Synthesis of kaolin catalyst assisted by molybdovanado phosphoric acid (MVPA@Kaolin)

To synthesize MVPA, around 22 g MoO₃ and more than 1 g V₂O₅ were mixed with more than 300 ml of distilled water in a round-bottom flask. After refluxing the mixture for an hour, three equal aliquots of more than 1.5 g phosphoric acid and more than 100 ml deionised water were added to the flask. After stirring the mixture continuously for 15 hours, a vivid orange-coloured solution was produced. The solution of MVPA (0.50 g in 50 ml distilled water) and 1.0 g of kaolin was continuously stirred to create a homogenous mixture. The water was then completely evaporated at 100 °C. The material was calcined for two hours at 500 °C after being dried for twenty-four hours at 110 °C in an oven. 3.3 g of MVPA@Kaolin were produced during the process. Using inductively coupled plasma-optical emission spectroscopy (ICP-OES) the elemental makeup of the catalysts was ascertained. MVPA exhibits as seen by its Mo/P ratio of 11.

2.2 Characterization of MVPA@Kaolin

Characterization has been carried out using powder X-ray diffractometer (with value of 10-80), FTIR, The BET surface area, Thermogravimetric analysis. The surface morphology of the material using transmission electron microscopy and scanning electron microscopy-energy dispersive X-ray.

2.3 Fluoride Adsorption by MVPA@Kaolin

The F⁻ removal was employed with the SPADNS technique [7]. The pH was adjusted to the proper value using either 0.1M HCl or 0.1M NaOH. The Fluoride removal efficiency in percentage:

$$\text{Percentage Fluoride Removal} = [(C_0 - C_t) / C_0] * 100 \quad (1)$$

where C₀ and C_t represented the starting concentration and the concentration (mol L⁻¹) at any point following the reaction's t (minute) run.

3 Results and dDiscussion

3.1 Analysis

3.1.1 Analysis through PXRD

Findings of the high-angle PXRD are shown in Figure 1 which also includes the MVPA/Kaolin and MVPA [6]. XRD peaks located at $2\theta = 18.1^\circ, 20.3^\circ, 22.6^\circ, 26.9^\circ, 29.1^\circ, 31.6^\circ, 38.0^\circ, 54.3^\circ,$ and 59.9° suggest that the MVPA has a notable level of crystallinity [9]. The material resulting in large angle reflection, as evidenced by the diffraction peaks of the MVPA@Kaolin at $2\theta = 10.7^\circ, 15.2^\circ, 18.6^\circ, 24.1^\circ, 30.7^\circ, 32.6^\circ, 36.1^\circ, 39.4^\circ, 43.9^\circ, 48.1^\circ, 55.7^\circ, 62.7^\circ,$ and 64.9° . The MVPA@Kaolin exhibits all of the primary reflections resulting from support, it can say that the kaolin was maintained.

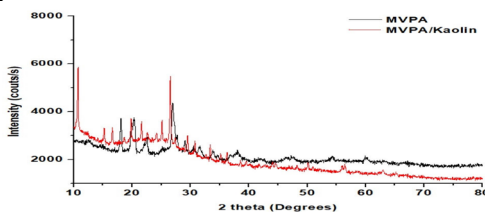


Fig. 1. Powder X-ray diffraction pattern of MVPA and MVPA@Kaolin.

3.1.2 Scanning Electron Microscopy (SEM)

The MVPA@Kaolin SEM micrographs are shown in Figure 2a. The 150 nm-sized kaolin found in the hybrid composite is responsible for crystalline structure seen in the picture of MVPA@Kaolin. Vanadium and kaolin bases were clearly visible in the EDX spectrum obtained from the exact location of MVPA@Kaolin (Figure 2b).

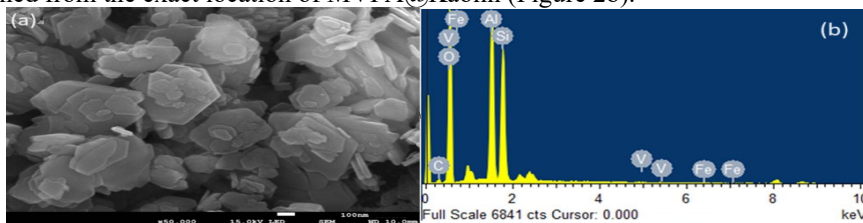


Fig. 2. SEM image (a) and EDX (b) of MVPA@Kaolin.

3.1.3 Transmission Electron Microscopy (TEM)

The material's well-organized structure was visible in the TEM pictures (Figure 3) of MVPA [5]. After MVPA functionalization, the composite material MVPA@Kaolin typically maintains the distinctive morphology of the support material.

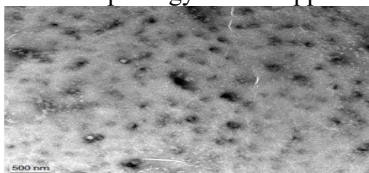


Fig. 3. TEM image of MVPA@Kaolin.

3.1.4 Thermo gravimetric analysis (TGA)

Thermogravimetric curves of the material from 25 to 900 °C revealed relatively small weight losses for MVPA, of roughly 61.5 percent (Figure 4). The weight loss in the temperature range of 28 to 900 °C indicates that there was a 23.5 % loading of MVPA in the MVPA/Kaolin hybrid composite [6].

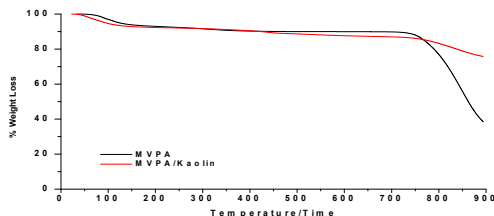


Fig. 4. TGA curves of MVPA and MVPA@Kaolin.

3.1.5 Nitrogen adsorption-desorption study

The BET surface areas of MVPA and MVPA@Kaolin are 3.0 and 14.9 m²/g, respectively (Table 1). Pore volumes of 0.005 and 0.079 cm³/g are found in MVPA and MVPA@Kaolin, respectively, with diameters of 83.2 and 158.0 (Å). The experimental findings may be interpreted as follows: the MVPA-modified material's surface and interior kaolin pores are filled with MVPA, and even after MVPA functionalization, the support structure remains unaltered [10-11].

Table 1. Nitrogen adsorption-desorption data.

Sample	BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	BJH Pore Diameter (Å)
MVPA	3.0	0.005	83.2
MVPA@Kaolin	14.9	0.079	158.0

3.2 Removal of Fluoride by catalyst

Defluoridation ability of the material was tested under various experimental settings. These parameters include temperature, solution pH, catalyst load impact, and reaction time.

3.2.1 Reaction time effect

The effectiveness of fluoride elimination was examined at various intervals of time 30, 60, 90, and 180 minutes and were found 78%, 79%, 81% and 85 % as the removal efficiencies. Figure 5 illustrates how the catalyst exhibited high fluoride removal efficiency as the contact duration rose. This was observed while stirring and monitoring the catalyst's effectiveness at various contact times.

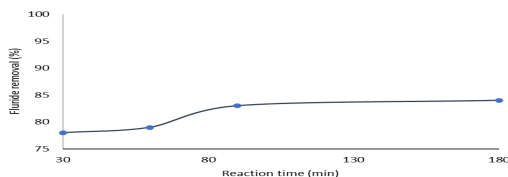


Fig. 5. Reaction time effect

3.2.2 Effect of pH

The removal efficiency was 84%, 80%, and 78% respectively (Figure 6) for 1, 5, and 9 pH [12]. The fundamental ideas of surface chemistry and ion exchange mechanisms explain the observed rise in fluoride removal efficiency in an acidic environment. The molybdovanado phosphoric acid catalyst supported by kaolin is expected to become more protonated on its surface in acidic conditions, which would increase the number of active sites available for fluoride ion adsorption. Furthermore, a higher adsorption efficiency could result from an enhanced electrostatic attraction between the positively charged catalyst and negative F⁻ ions in an acidic environment.

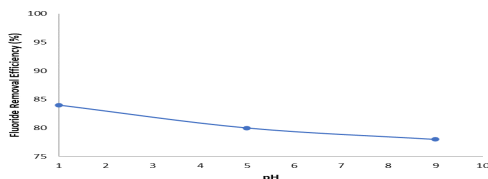


Fig. 6. pH effect for Fluoride removal

3.2.3 Catalyst load influence

Effectiveness of catalyst in removing fluoride was examined at various loading. For MVPA@Kaolin, the removal efficiencies were 67%, 80%, 85 % and 85% at 2g/L, 4g/L, 5g/L and 8 g/L. The catalyst demonstrated a consistent rise in fluoride removal efficiency as the catalyst load increased, according to the results displayed in Figure 7.

3.2.4 Influence of temperature

The influence of the catalyst observed at varying temperatures of 30 °C, 50 °C and 80 °C (Figure 8). The efficiency of the catalyst was moderate at 30 °C (81%) for MVPA@Kaolin catalyst. However, higher fluoride removal efficiency by the catalyst was observed at 50 °C (85 %) remained almost constant as the temperature was raised to 80°C (85%). The efficiency did not change even at 80°C, indicating that although the catalyst is efficient at higher temperatures, it loses its effectiveness at temperatures over 50 °C. Elevated temperatures may stimulate the catalyst's activation, hence enabling more interaction with fluoride ions. The catalyst's active sites may have reached saturation, which prevents additional adsorption when all accessible binding sites are taken up, explaining the removal efficiency plateau that appears above 50°C. Furthermore, exceedingly high temperatures may cause the catalyst's structure to alter or the desorption of fluoride ions that have already been adsorbed, which would prevent future efficiency gains.

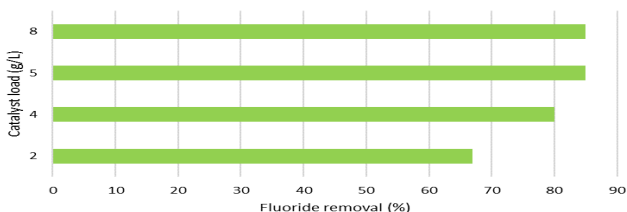


Fig.7. Catalyst load influence

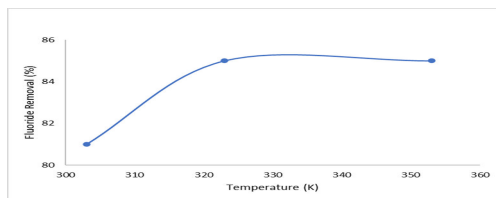


Fig. 8. Temperature effect for fluoride removal in water

4 Reusability of MVPA@Kaolin

Further investigation on the reusability of the catalyst was carried out. It was observed that the catalyst proved to be reusable for up to four different runs (Figure 9). This was achieved by collecting the catalyst that was used in the first place, allowed to dry, and used it again. The stable performance over time improves the catalytic process' overall effectiveness and cost-effectiveness.

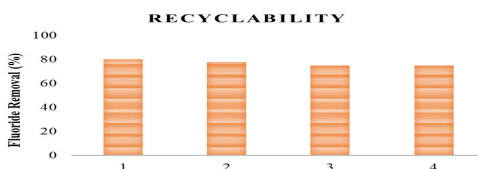


Fig. 9. Reusability of MVPA@Kaolin.

5 Conclusion

During the fluoride removal procedure, several parameters of temperature, pH, reaction time, and catalyst load were examined. Under ideal circumstances, the catalyst showed good fluoride removal efficiency. The ideal reaction parameters were 50 °C, pH 5, 4g/L of catalyst load, and 30 minutes of reaction time. At ideal conditions, the fluoride removal efficiency was 85 %, indicating that these catalysts had a good capacity for adsorbing fluoride. This work offers a fresh insight into the treatment of water-related problems by using a biodegradable, inexpensive, and ecologically acceptable chemical that is typically considered waste.

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