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Kinetics, equilibrium, and thermodynamic aspects of removal of fluoride from drinking water using meso-structured zirconium phosphate

Abstract

This paper covers the creation of meso-structured zirconium phosphate (MZrP) for fluoride removal from drinking water. The produced material was evaluated, and the kinetics of fluoride removal from aqueous solution were investigated using batch mode. The effects of solution pH, starting fluoride concentration, material amount, and temperature on fluoride removal kinetics were investigated in detail. The findings of four kinetic models fitted to the experimental data demonstrate that the pseudo-second order model provides a better description of the uptake process. Thermodynamic characteristics, including enthalpy (ΔH) and entropy (ΔS), were calculated to be 44.79 kJ mol−1 and 0.223 kJ mol−1 K−1, respectively. The negative value of ΔG indicates that adsorption is feasible and spontaneous. MZrP can be regenerated for future use, having been tested for five cycles of operation.

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Introduction

The presence of fluoride in drinking water piques people's interest because of its significant influence on living organisms' physiological systems [1,2]. Excess fluoride in drinking water has been recorded in numerous nations, including China, Pakistan, Bangladesh, Thailand, and India. Drinking water with a high fluoride level might cause mottling of teeth and weakening of bones and ligaments. The World Health Organization (WHO) guidelines restrict fluoride levels in drinking water to 1.5 mg L−1 [3]. Fluoride contamination in ground and surface water can be caused by many geochemical sources, including fluoride-containing minerals and deposits in the earth's crust [4]. Manyuntreated industrial effluents include fluoride, which is hazardous to aquatic bodies. Among numerous commercially available approaches for decontamination of fluoride. Zirconium has a recognized affinity for fluoride. Meso-structured zirconium phosphate (MZrP) is a promising material for evaluating fluoride removal due to its unique structural properties and lack of prior research on its use. The preparation of meso-structured zirconium phosphate with high specific surface area has been described in a restricted method.

The current research aims to produce, describe, and assess the fluoride adsorption properties of MZrP. The material was characterized using FTIR, SEM combined with the Energy Dispersive Spectrum (EDS)

Technique, Transmission Electron Microscope (TEM), and X-Ray Diffractogram (XRD). BET surface area was measured using the Quantachrome automated gas sorption device. The batch adsorption tests were carried out with different starting fluoride concentrations, adsorption contact times, pH, and medium temperatures. A specific goal of the investigation is to analyze both the kinetic and thermodynamic elements of the adsorption process, which can be useful in determining the adsorbent material's future economic feasibility. The experimental data were fitted to Freundlich, Langmuir, Dubinin-Radushkevich (D-R), and Temkin isotherm equations to determine the best-fitting equation. The elution of fluoride from the adsorbent material, as well as the material regeneration capabilities, were examined to indicate a sustainable deployment. Furthermore, the adsorbent material was employed to remove fluoride from groundwater samples obtained in a fluoride-endemic location.

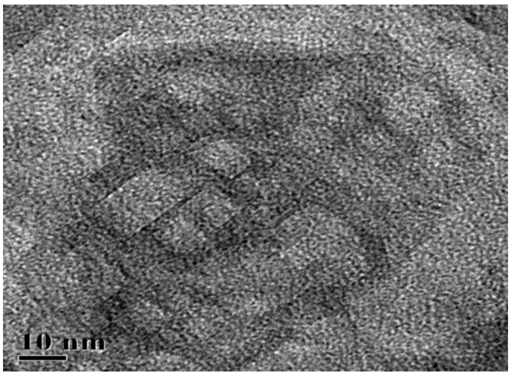

Fig. 1. Transmission Electron Microscope (TEM) of meso-ZrP.

1. EXPERIMENTAL

1.1. Preparation of adsorbent material

It described a technique for manufacturing mesoporous Zr-phosphate. To dissolve 1.79 g of ZrOCl2•8H2O in 100 mL of distilled water, add 3.78 g of solid (NH4)2CO3 while stirring continuously. Then, 1.47 g of (NH4)2HPO4 was added to the solution, followed by 0.61 g of tetradecyltrimethylammonium bromide (TTBr) while stirring continuously. The solution was maintained in a closed polypropylene bottle and incubated at 80°C for 72 hours. The tests were done with variations of adsorbent dosage, fluoride concentration, contact time, pH, and temperature to find the optimal experimental conditions of fluoride.

1.2. Analytical measurements

The FTIR spectra of all sample materials were recorded using a Shimadzu IR Prestige-21. The sample was examined with a Hitachi H-800 transmission electron microscope (TEM) from Japan. A scanning electron micrograph (SEM) of the sample material was produced using a Jeol (JSM 6390 LV) device in conjunction with energy dispersive spectroscopy. The isoelectric point was found using a Malvern Zeta meter (Model Nano ZS). The Shimadzu XD3A diffractometer (40 kV/30 mA) was used to acquire an X-ray diffraction pattern in the 2θ range of 1.5-70◦ and wavelength of 1.54 A˚ using nickel-filtered CuKα radiation. BET surface area was measured using the Quantachrome automated gas sorption device. The concentration of fluoride in the solution was determined using the Orion 720 A+ Ion analyzer.

1.3. *Sorption studies*

The batch experiment involved introducing a fixed amount of adsorbent material to 100 mL of test solution in a conical flask that was shaken for a set amount of time. At a room temperature of 25 ± 2 ◦C, a 200 rpm rotation was maintained. All trials had an initial fluoride concentration of 10 mg L−1, except for those examining its consequences. The pH of the solution was changed with either HCl or NaOH. To test the reusability of adsorbent material, 0.8 g was added to 100 mL of 10 mg L−1 fluoride solution. The adsorbent was filtered and vacuum-dried in an oven at 70°C. The dried adsorbent material was then used repeatedly to assess the amount of fluoride adsorption. NaOH was used to conduct further desorption studies on the fluoride adsorbed adsorbent. It should be noted that each data point is the average value of triplicate readings.

2. Results and discussion

2.1. Characterization

FTIR is a significant tool for material characterization. The FTIR spectrum of MZrP reveals a strong peak at 1050 cm−1 due to P-O stretching vibrations. The peak at 2400 cm−1 represents the stretching vibration of the P-O-H bond, whereas the wide band at 3500 cm−1 represents the asymmetric OH stretching vibration of the water molecule. The faint signal at 1650 cm−1 indicates the bending vibration, ı(O-H), of water molecules. The peak at 746 cm−1 corresponds to the P-O-P symmetric stretching vibration band. Figure 1 shows the TEM micrograph of the substance. The connectedness between various particles might be attributable to condensation processes between hydroxyl groups on nearby particles during the aging or calcination process, resulting in agglomeration. The material's X-ray diffraction pattern (Fig. 2) reveals a sharp peak at 2θ of 1.2◦, indicating a meso-structured material. The interlayer spacing was determined to be 7.3 nm, which corresponds to the distinctive diffraction pattern of a mesoporous structure. The surface morphology of fluoride adsorbed MZrP is illustrated in Fig. 3. The material shows features related to agglomeration of particles. The corresponding EDS spectrum (embedded in figure) shows signals generated from elements present at surface of the adsorbent material. The signals show the presence of elements such as P, O and Zr, Na and F in the material. The P/Zr molar ratio was eval- uated to be 1.64. The presence of Au signal in the spectra resulted from the gold material that purposely coated to increase the elec- trical conduction, hence to improve the quality of micrograph. The surface area of meso-structured ZrP, determined by BET technique,was found to be 129 m^2 g^{-1}

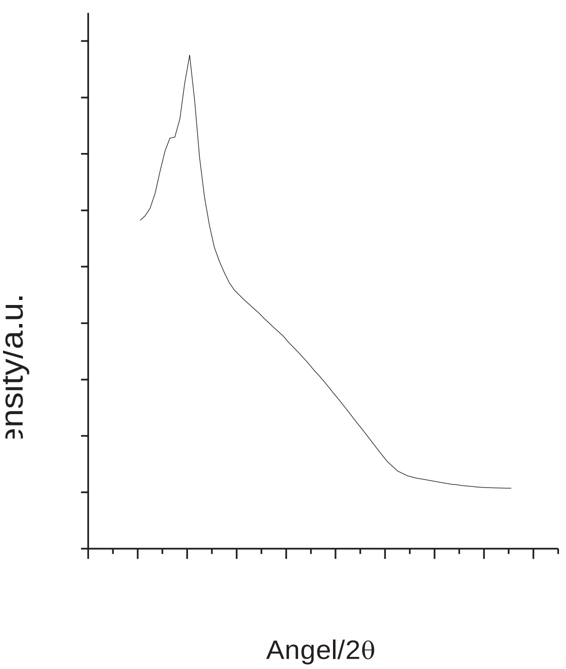

Fig. 2.X-ray diffractogram of meso-ZrP showing Meso-porous characteristics

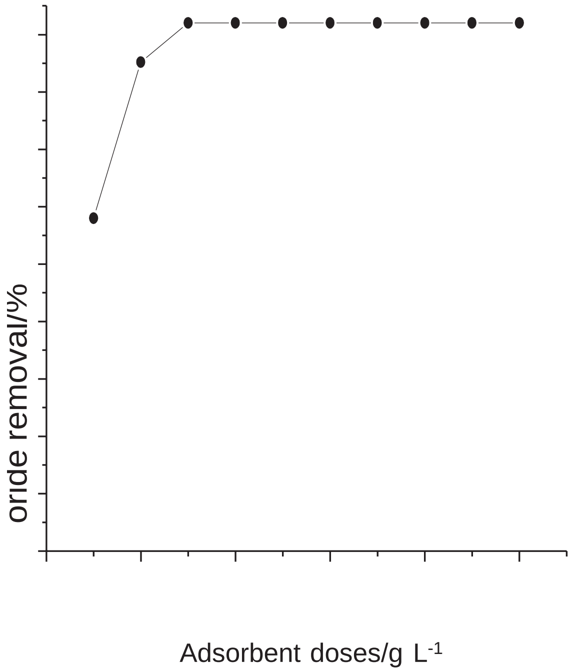

Fig. 4. Variation of adsorbent dose, 10 mg L^{-1}; time of contact: 60 min.

Figure 3 shows the surface morphology of fluoride-adsorbed MZrP. The material exhibits particle aggregation characteristics. The matching EDS spectrum (shown in the picture) displays signals created by components on the surface of the adsorbent material. The signals indicate the existence of elements like P, O, Zr, Na, and F in the substance. The P/Zr molar ratio was determined to be 1.64. The existence of an Au signal in the spectra was caused by the gold material being purposefully coated to boost electrical conductivity and so improve the quality of the micrographs. The surface area of meso-structured ZrP measured by BET method was 129m2g−1.

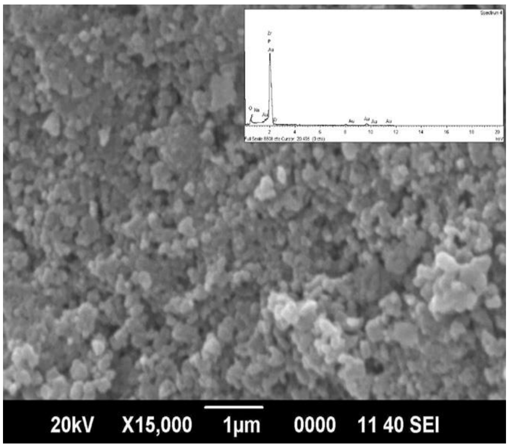

Fig. 3. Scanning Electron Micrograph (SEM) of fluoride adsorbed meso-ZrP embedded with corresponding EDS spectra showing corresponding elemental com-position

2.2. *Effect of initial fluoride concentration*

The fact that when the concentration or amount of fluoride in solution gradually increases and the adsorbent amount remains constant, the adsorbent's binding ability approaches saturation, resulting in an overall reduction in fluoride removal. This might be because fluoride ions occupy available surface space. The adsorption process was mathematically confirmed using several adsorption isotherm models. Thus, the equilibrium connection between adsorbent and adsorbate is best characterized by the adsorption isotherm.

The Freundlich expression is an exponential equation that posits that the concentration of adsorbent on the adsorbate surface grows in proportion to the adsorbent concentration. In theory, these formulas allow for unlimited adsorption. This equation is extensively used to describe heterogeneous systems, which are defined by the heterogeneity factor 1/n.

$$q_e = K_F \; C^{1/n}$$

where, K_F and 'n' are the Freundlich constants that indicate the relative capacity and adsorption intensity, respectively. The values of K_F and 'n' are obtained, respectively, from the slope and intercept of the plot between ln q_e and ln C_e of the linearized Freundlich equation. Further it also describes the adsorption is characterized by uniform distribution of binding energies. The linearized form of Temkin isotherm is represented by the following equation

$$q_e = B_1 \ln A + B_1 \ln C_e$$

The equilibrium binding constant (L mol−1) represents the highest binding energy, whereas the constant B1 is connected to 1RL = (1 + K C) (18) heat of adsorption. A plot of qe vs. ln Ce allows you to calculate the constants B1 and A based on the slope and intercept. However, the isotherm constants for the Langmuir and Freundlich isotherms provide little insight into the adsorption mechanism. To further understand the kind of adsorption, the equilibrium data was examined using the D-R isotherm. The D-R isotherm can be expressed as

$$q_e = q_m \exp(-K\varepsilon^2)$$

2.3. *Evaluation of thermodynamic parameters*

Higher temperatures were found to promote fluoride elimination within the study's stated range. The values of the thermodynamic parameters were computed. Negative ΔG◦ readings at all temperatures demonstrate fluoride sorption is spontaneous and easier at higher temperatures. The reason might be that the adsorption of fluoride ions onto the surface of the adsorbent material is promoted by the removal of water molecules previously attached to the surface of the adsorbent, resulting in an increase in the entropy factor. Other writers noticed a similar tendency as well. Positive values for ΔH◦ and Ea indicate an endothermic sorption process. A positive value of ΔH◦ suggests increased unpredictability during the sorption process.

2.4. *Effect of other ions*

The effects of different ions and competing co-ions on fluoride adsorption were studied in the presence of sulfate, nitrate, chloride, bicarbonate, and phosphate .The experimental condition for starting fluoride concentration was fixed at 10 mg L−1, whereas the initial concentration of co-ions ranged from 25 to 600 mg L−1. Figure 11 illustrates that NO3−, Cl−, and SO42− had minimal influence on fluoride removal operations.

The defluorination capacity of adsorbent material was examined using ground water samples collected from Boden block, Nuapada district, Orissa, India. The synthetic water samples were created by adding sodium fluoride to deionized water. It displays the outcomes of the experiment. It was discovered that more fluoride could be removed from synthetic water samples than from groundwater samples. The explanation for this might be that actual ground water samples include a wide range of cations and anions, which could interfere with the standard adsorption procedure. displays a variety of metrics derived from collected ground water samples, such as pH, total hardness, alkalinity, and so on.

The impact of adsorbent dosage on fluoride removal was examined at an ambient temperature of (25 ± 2) ◦C and contact duration of 60 min. The initial fluoride concentration in the solution was maintained at 10 mg L^{-1}. The proportion of fluoride removed rises with increasing adsorbent dosage. With a dosage of 3.0 g L^{-1}, meso-structured ZrP effectively removes about 96% of fluoride. This might be attributable to the abundance of surface area and hence adsorption sites. Aside from that, the porous structural characteristic may enhance the adsorption process by allowing anions to diffuse into the material.

2.5. Reuse of adsorbent

Effective reuse of adsorbent material has a direct impact on its cost factor and hence usefulness in continuous batch adsorption operations. The percentage of fluoride adsorption was determined to be 96.0%, 88.0%, 75.0%, 62.0%, and 51.0%, respectively, for the first, second, third, fourth, and fifth cycles of batch operation.

Desorption tests were also conducted, and the results showed that fluoride desorption from the adsorbent was 70.0% and 86.0%, respectively, while employing 0.001 and 0.1 M NaOH solutions. The results suggested that the adsorbent was sustainable and useful for commercial use.

2.6. **Conclusion**

MZrP serves as an adsorbent material for removing fluoride from aqueous solutions. The structural characteristics may be primarily responsible for fluoride elimination efficiency. MZrP exhibits maximal fluoride adsorption at pH 6.0, indicating that the material may be used to decontaminate drinking water from fluoride at the medium's natural pH. A probable mechanism of the adsorption process was hypothesized based on pH and zeta potential measurements. Mathematically, the adsorption process was validated using various adsorption isotherm models and error analysis to determine the best-fit one. The energy (E) per mole of the adsorbate analyzed using D-R isotherm was determined to be 8.77 mol2 kJ^{-2}, indicating that Adsorption may occur through an ion-exchange process. The positive value of ΔH shows increased randomness throughout the sorption process. Diverse ions had minimal influence on fluoride removal, allowing for successful utilization of adsorbent material in a competitive ion environment. Fur-The usage of 0.1 M NaOH was shown to be quite successful in leaching. As fluoride is absorbed from the material surface, the adsorbent may sustainably use for several cycles. This paper demonstrated a potential utility of MZrP for fluoride removal, and hence it is hope to discover applications in tapping new prospects, such as the creation of novel fluoride-specific adsorbent materials. Designing a new fluoride removal kit for effective and ecological use.

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