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Application Of Modified Mine Waste For The Sustainable Management Of Fluoride In Drinking Water

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***Abstract*:**

Waste rocks obtained from mining operations are typically stockpiled due to the lack of their economic value. This practice resulted in significant land occupation and potential for secondary pollution risks due to the lack of probability of leaching. This study investigates the potential use of waste rocks as a new type of adsorbent for groundwater that is enriched in fluoride. Ferrous chloride was added to shale, a coal mining refuse, at a 3:1 ratio to change its chemical makeup. By using batch adsorption, the adsorption process was optimised. Using energy-dispersive X-ray (EDS), X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectrophotometer (FTIR), the adsorbent's surface morphological characterisation was carried out. The best results were obtained when polluted water was defluoridated for 60 minutes at a neutral pH using 100 mg/L. A 32% clearance efficiency was achieved at a 10 ppm fluoride contamination level. Post characterization and optimization the adsorbent was tested for Langmuir and Freundlich isotherm together with kinetics pseudo first and second order to ensure its adsorption capacity.

Keywords: mine waste, shale, defluoridation, adsorption, groundwater.

1. Introduction

Around the world, groundwater is a key source of drinking water. But access to safe drinking water is becoming more and more difficult due to geogenic factors and anthropogenic activity and excessive demand. One of the most dangerous geogenic pollutants, fluoride, is reported to be endemic in 22 of India's 28 states. Rocks like granite, basalt, shale, and minerals like biotite, topaz, cryolite, fluorite, and fluorspar naturally dissolve fluoride (Kumar et al 2022). Industrial waste, glass and ceramic discharge, semiconductor manufacturers, iron factories, brickworks, and aluminium smelters are examples of anthropogenic sources. Fifty percent of the people in Uttar Pradesh consume too much fluoride, especially in the southwest where there has been an increase in mining activity (Ahamad et al 2021). According to reports, 50–90% of the stone that is extracted is wasted during the mining process as scrap or slurry (Singhal et al 2009). This indicates that the mining process produces a large quantity of waste. Stone debris has multiple uses in different industries, such as building material, embankment construction, road construction, and pottery production (Biswas et al., 2016). Shale is a sedimentary rock that is mostly produced by the mining and washing of coal (Zhao and Xiang, 2009). Shale is widely distributed across the earth's crust and is made up of both organic and inorganic materials, including minerals with adsorption properties as kaolinite, illite, and smectite (Hamdi and Sarsa, 2009). Shale is reported to contain highly charged cations including iron and aluminium (Sadhu et al 2013). Physical and chemical changes can affect shale's capacity for adsorption (Biswas et al., 2016). In addition to providing an environmentally benign treatment alternative, using shale as a free raw material for the adsorption of fluoride from groundwater will aid in the management of coal mine waste.

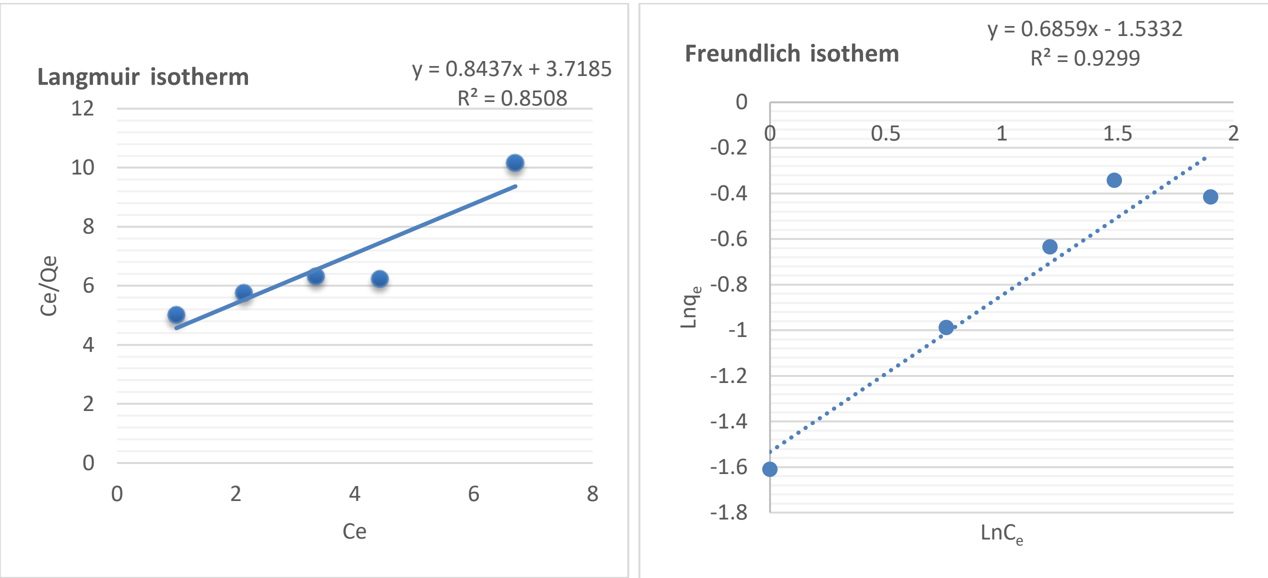
2. Materials and Methods

The shale samples used in the study were obtained from the Department of Geology, School of Earth and Environment Sciences, Babasaheb Bhimrao Ambedkar University (26˚45' 52" N 80˚ 55' 45" E) Lucknow, Uttar Pradesh, India. Shale samples were washed, crushed, and sieved to obtain a fraction of ≤250 µm for adsorption purposes. Adsorbent was prepared by chemical pre-treatment of shale with ferrous chloride (3:1 w/w) followed by pyrolysis in a muffle furnace (ICON Instruments Company, India) at 800 °C with retention time of 1 hr. the Characterization and optimization of adsorbent was performed by SEM-EDX,FTIR,XRD followed by batch adsorption study(Kulsoom et al 2024).

3. Result and discussion

3.1 Modelling of Adsorption isotherm and Kinetics

The results obtained were tested against Freundlich and Langmuir isotherm constants to understand adsorbent and adsorbate interaction and kinetics models for rate of reaction respectively.



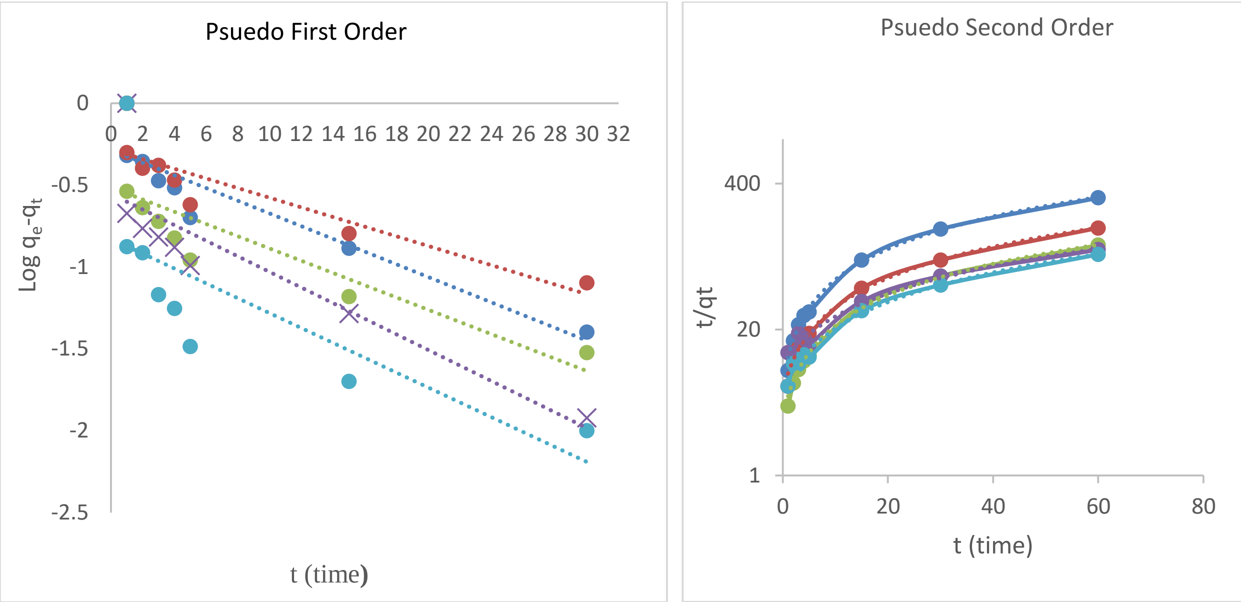
(a) (b)

Figure 1: Linear graphs of Kinetic parameters for adsorbent.

Table 1: Isotherm study applied on chemically modified adsorbent.

Adsorption isotherm model	Equation	Parameters
Langmuir isotherm	$q_e = (Q_{max} * K_L * C_e) / 1 + K_L * C_e$	$K_L = 3.71$ $R^2 = 0.8508$
Freundlich isotherm	$q_e = K_f C_e^{1/n}$	$n = 1.5332$ $R^2 = 0.9299$

The results proved that the adsorbent followed Freundlich isotherm (R2 = 0.9299) more closely than Langmuir isotherm (R2 = 0.8508) which implies multilayer adsorption of fluoride over a homogenous carbonated sorbent (Table 1and Figure 1). This data was supported by the experiment conducted by Behra and Sahu 2022, Behra and Sahu 2023 by using heat modified mine waste (shale) to defluoridate groundwater.



(a) (b)

Figure 2: Linear graphs of Kinetic parameters for adsorbent.

Table 2: Kinetics study applied on chemically modified adsorbent

Kinetics reaction	Parameters	Fluoride concentration				
		2ppm	4ppm	6ppm	8ppm	10 ppm
Pseudo first order	q_e K_1 R^2	12.5 0.08 0.56	6.45 0.15 0.78	8.54 0.117 0.66	27.02 0.03 0.80	18.18 0.05 0.86
Pseudo second order	q_e K_2 R^2	0.202799 4.931 0.99	0.384 2.603 0.99	0.540 1.848 0.99	0.636 1.571 0.99	0.679 1.472 0.99

For adsorption kinetics study, 50 mgL^{-1} of adsorbent was added to varying fluoride concentration (2, 4, 6, 8, 10 ppm) with varying time interval (5-180 mints). The residual concentration of fluoride as a function of time shown in Table 2 and Figure 2. The results concluded that the adsorbent followed pseudo-second order kinetics more accurately reflecting chemisorption of fluoride over the surface of adsorbent

Conclusion

Chemically treating shale, an inexpensive, environmentally benign, economical, and waste-utilized adsorbent was tested for its removal efficiency. This study offers a simple way to fight fluoride contamination in drinking water. The adsorbent's validity was demonstrated by chemical and physical characterization followed by several batch tests and optimization of adsorbents dose, pH, concentration and time for best results. As a result, adsorbent made from waste materials can be a viable and long-term option for groundwater fluoride and mine waste management.

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