



Research article

Coal mine waste characterization and defluoridation property

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ABSTRACT

Fluoride contamination has been addressed as a major problem worldwide, along with the scarcity of water. This attracts researchers to do more research in the field of fluoride contamination and mitigation of high fluoride content in water. There are various studies, that used a variety of adsorbents for the removal of fluoride from contaminated water. But none of them utilized the vast number of waste, that is generated from the coal mining industries. In this paper, Shale, which is a common coal mine waste, has been used as an adsorbent for fluoride removal from aqueous solution. Along with the defluoridation property of shale, the effect of weathering on the adsorption property of shale was also analyzed using different characterization tests, such as XRD (X-ray powder diffraction), SEM (Scanning Electron Microscope), and FTIR (Fourier Transform Infrared spectroscopy). Two types of shale samples were collected, crushed, and used in the adsorption process in the lab using synthetic fluoride solution. The maximum efficiency of type I (**weathered**) shale was obtained as 47.05% compared to type II (**fresh**) shale as 40.02% for 3 ppm initial fluoride solution for 60 min of contact time in pH range 5–7 using batch adsorption process. Other parameters such as shale particle size, pH, and total suspended solid present before and after the adsorption process were also taken into consideration. The adsorption followed pseudo-second kinetics and Freundlich isotherm with an adsorption capacity of 23.66 mg/g, and 21.33 mg/g for weathered and fresh shale respectively. The characterization test showed more clayey content in the weathered shale compared to fresh shale, making it more porous and suitable as a fluoride adsorbent. XRD showed the F⁻ containing minerals such as Villiumite (5.1%) and Fluorite (4.3%) in F⁻ loaded weathered shale, confirming the F⁻ adsorption onto the shale surface. The major advantage of shale over other existing adsorbents is, it removes the fluoride without significant change in pH, and there are no or very less suspended ions that can be found in treated water. This means the water may not need any secondary treatment after the adsorption process. Shale is a very common and readily available mine waste, that is used for the ceramic industry, building materials, and road construction, making it a no-cost material to be used as an adsorbent for fluoride removal.

1. Introduction

During the coal mining, substantial quantity of shale is generated and they constitute the overlying or underlying strata or low grade material and is discarded as waste. The abundance of this waste is vast in mining majority country like India. Shale is the most

Abbreviations: MCL, Mahanadi coalfields Ltd..

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Nomenclature

Type I	Weathered shale
Type II	Fresh shale
WHO	World Health Organization
IS	Indian Standard
NTU	Nephelometric Turbidity Unit
FTIR	Fourier Transform Infrared spectroscopy
SEM	Scanning Electron Microscope
XRD	X-ray powder diffraction

common sedimentary rock, accounting for about 70% of the rock in the Earth's crust. Shale is a clastic sedimentary rock, mainly composed of 50–90% of ash, and nearly 30% of clay [1]. Proper management of this waste can be done by using it for construction purposes, dumping it on slopes/ embankments, or it may be used for different water treatment purposes with proper modification. Shale mainly contains clay and quartz, which were found to be better adsorbents for fluoride. The effect of various weathering parameters such as exposure to heat and cold, along with the high pressure in the earth's crust influence the mineral component of the shales. The color of shale varies from grey, and yellowish to dark black depending on the material composition in a particular type of shale. For example, the presence of high organic matter and weathering collectively affect the color of shale making it black (carbonaceous shale). Till date, there are no studies on the defluoridation property of weathered coal shale. This paper is highly focused on the adsorption of F^- from aqueous solution using weathered coal shale compared to fresh shale, along with the characterization of these two types of shales to go deep into the effects of weathering on their mineralogy.

Fluoride is a naturally available material that can be found in soil, water, and plants in some quantities. It is also an essential component for the formation of teeth and bone. The permissible limit for fluorine in drinking water should be within 1.5 mg/L as per WHO (World Health Organization) guidelines. Continuous exposure to excess fluoride in our body can affect bone density, bone structure, and cause tooth decay [2]. Many countries have regions where the water has a fluoride content of more than 1.5 mg/L [3]. The most common effect due to fluoride exposure is fluorosis. In India Rajasthan, Gujarat and Andhra are worst affected due to fluorosis [4]. In India high concentration of fluoride has been observed in many coal mining areas [18–20].

Currently, methods used to remove fluoride are mainly adsorption, precipitation, membrane separation, and electro-sorption. The precipitation method mainly uses alum or calcium salts. It is very effective for fluoride removal but it affects the pH, and leaves a residue of salts and suspended particles in the treated water. That may need another method to remove these particles from treated water. Out of all the above methods, Adsorption is the most efficient, economic, and low-skill labor experiment for defluoridation. The efficiency of any adsorption technique depends on its adsorbent. In past decades, many adsorbents have been in use for defluoridation. For example, natural banana peel [5], Dry Biomass [6], Clay powder Rice Husk [7], Bone char [8], clay [9], Low-grade coal [10], Oyster shells [11], bentonite clay [12], Raw and modified cement clay [13] have been used successfully for defluoridation. But with a higher initial fluoride concentration, more adsorbent dose is required as the adsorbent loses the adsorption capacity. They also need a certain pH range to be used most efficiently. In this paper, a new waste from coal mining is used as an adsorbent for defluoridation.



Fig. 1. New shale sample collection.

2. Materials and methods

2.1. Fluoride solution preparation and testing using pH/ISE

Fluoride Stock solution was prepared using 100 ppm standard F^- solution (Thermo Scientific). Fluoride standards in the range of 1–10 mg/L were prepared by adding the appropriate amount of distilled water to set 100 ml of solution. TISAB III was used for the determination of fluoride concentration in solution after the adsorption process. 5 ml of standard TISAB III solution (Thermo Scientific) was used for 50 ml of the sample each time before testing in the pH/ISE meter. The chemicals used were of analytical grade throughout the whole process.

2.2. Adsorbent collection and preparation

To compare the effect of different shale characteristics on the adsorption process, two types of shale samples were collected from the Samleswari open-cast project located in the IB valley coalfields of MCL mine, Odisha as shown in Figs. 1 and 2. **Type I** shale was 5–10 years old and **type II** was freshly excavated shale from the mine. Shale samples were collected in dry polythene bags, washed and dried at room temperature to remove unwanted dust particles from the surface. The samples were then crushed manually and sieved as per IS (Indian Standard) 469/1972 to get the sizes 1.18 mm, 0.600 mm, 0.425 mm, 0.250 mm, 0.212 mm (Retained), and 0.212 mm (passing) shown in Fig. 3, Fig. 4, and Fig. 5.

3. Characterization of adsorbent

The adsorbent characterization was done to find the mineralogical composition along with the functional groups present in the particle which helps with its adsorption property. The characterization was done with FTIR, SEM, and XRD for both types of shale samples before and after fluoride loading.

3.1. Characterization using FTIR

FTIR study for both types of shale samples with and without fluoride loading was done. The FTIR graph is shown in Fig. 6 for type I shale without fluoride loading and Fig. 7 without fluoride loading. The FTIR graph of Type I shows four peak numbers at 728, 1036, 3675 and 3689 representing C–Cl (strong) and –OH (strong and sharp) bonds respectively. After being loaded with fluoride, OSS shows three peaks at 724, 1026, and 3693 representing C–Cl (strong), C–F (strong), and –OH, –H (strong and sharp) bonds. The three main adsorption regions of shale are $3000\text{--}3800\text{ cm}^{-1}$, $1000\text{--}1300$, and $500\text{--}1000\text{ cm}^{-1}$, and notable differences can be observed in each region of raw and F^- loaded shale. The band between 3660 and 3690 cm^{-1} could be described as stretching vibrations of structural groups-groups of Shale and water. At low-frequency below 1000 cm^{-1} , shale showed a strong band and broadband, this could be due to stretching and vibration of the Si–OH group. Band 1036 and 728 cm^{-1} could be attributed to Al–OH–Al, Al–O, and Si–O vibrations indicating the presence of quartz. Reduction in absorbance intensity in F^- loaded shale was recorded. This attributes to the fact that structural hydroxyl groups and water molecules contributed to F^- adsorption process through the exchange of OH^- in Al, Si oxides for F^- .

FTIR graph of Type II as shown in Fig. 8 have three peaks at numbers 628, 1034, and 3689 representing C–Cl (strong) and –OH (strong and sharp) bonds respectively. After being loaded with fluoride the FTIR graph (Fig. 9) shows two peaks at numbers 620, and 1032 representing C–Cl (strong) as shale being a mineral contains chloride in its natural form. The disappearance of –OH (strong and



Fig. 2. Old shale sample collection.



Fig. 3. Shale sample crushing.



Fig. 4. Sieving of sample.



Fig. 5. Different size sample.

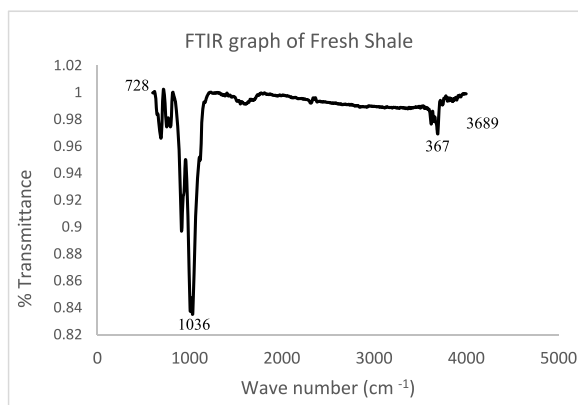


Fig. 6. FTIR of type I without fluoride loading.

sharp) bonds may be due to the replacement of these bonds by Fluoride [14].

3.2. Characterization using SEM

SEM Characterization was done to explain the porous and size of the particle. SEM was done on two types of shale before and after fluoride loading. The result is shown in Figs. 10 and 11 for type I shale compared to the SEM result obtained for type II shale in Figs. 12 and 13. The pore size and number are visibly more in type I shale before F⁻ loading explains the higher adsorption capacity of type I compared to type II. After the loading of F⁻ onto the adsorption site there is a smoothing effect of fluoride ion on the pore sites which confirms the adsorption.

From the SEM image, we can compare and obtain the minerals present on the adsorbent's site. From Fig. 14 we can see the presence of organic pores, quartz, clay, silicates, calcite, and pyrite mineral on the shale site. The main reason shale can be used as an adsorbent is the presence of clay and organic pores that help in the adsorption of fluoride ions onto shale's active sites.

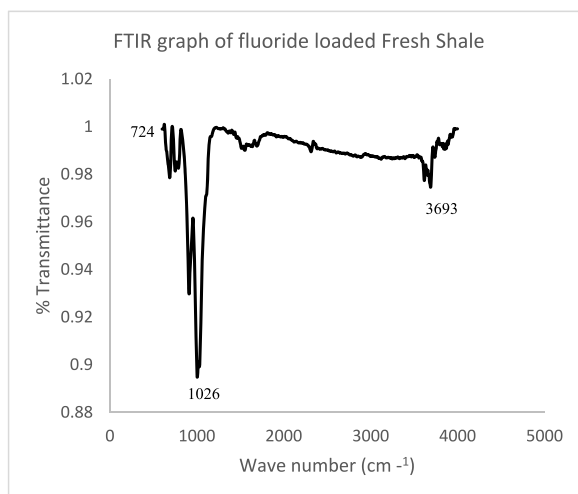


Fig. 7. FTIR of type I with fluoride loading.

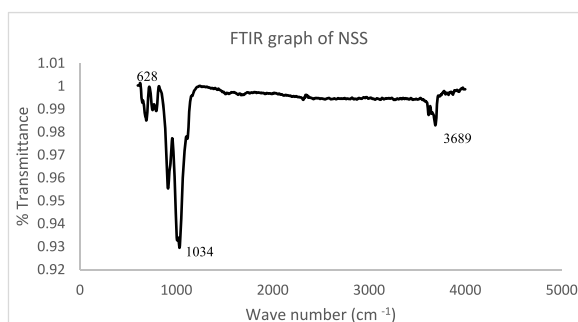


Fig. 8. FTIR of type II without fluoride loading.

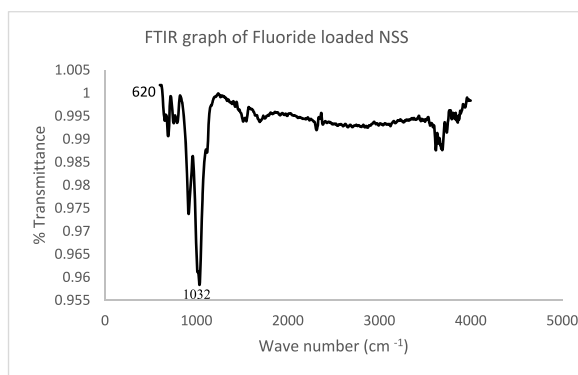


Fig. 9. FTIR of type II with fluoride loading.

3.3. Characterization of adsorbent using XRD

X-ray diffraction is a common technique for studying crystal structures, atomic spacing, and mineral identification. We utilized this technique to identify minerals in our shale sample. The sample was powdered and the XRD apparatus was utilized at our institute for mineral identification. The resultant graph was analyzed in Match software for mineral phase classification. The result obtained shown in Table 1 can be explained as the shale mostly contains clay minerals like Kaolinite and Illite that helps the adsorption process for fluoride. After loading with F⁻ we can see the fluoride-containing minerals were found in the adsorbents confirming that adsorption has taken place for both types of shale.

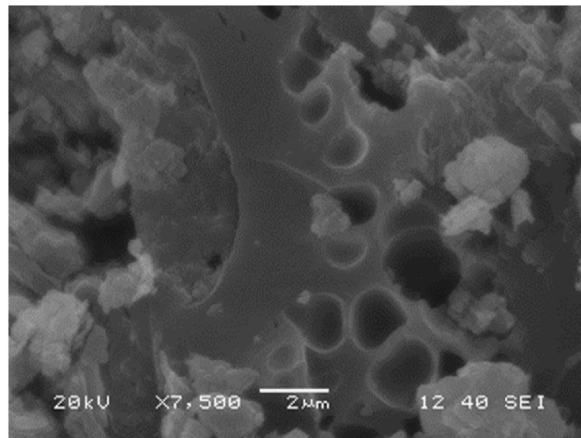


Fig. 10. SEM of type I before F- loading.

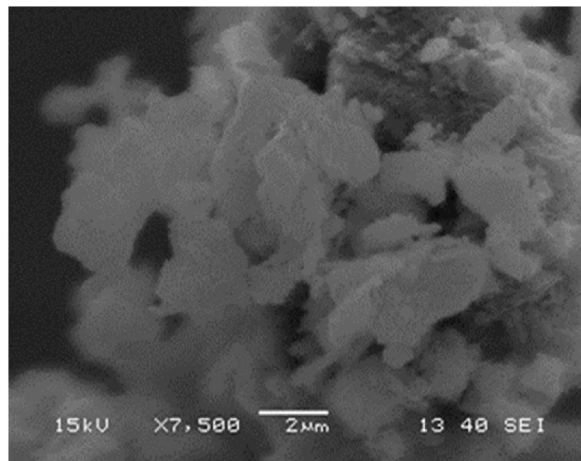


Fig. 11. SEM of type I after F- loading.

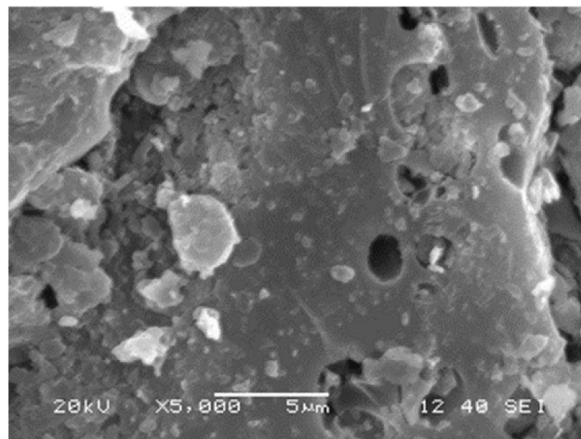


Fig. 12. SEM of type II before F- loading.

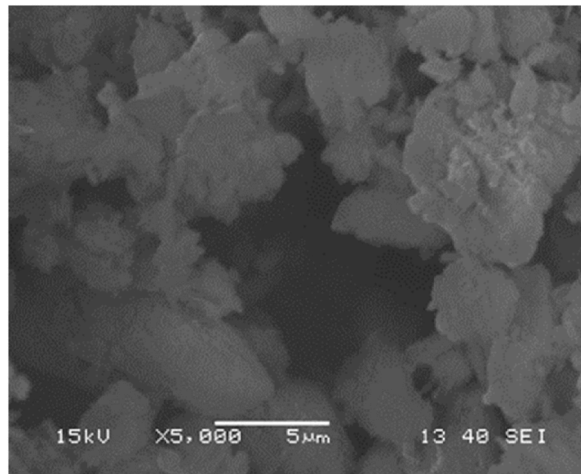
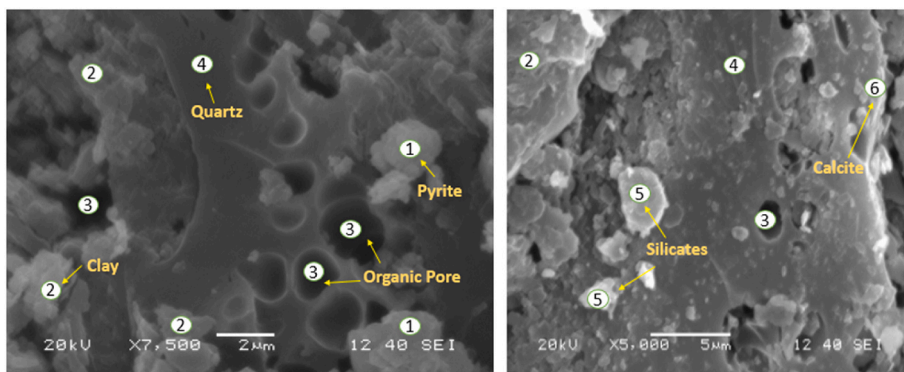


Fig. 13. SEM of type II after F- loading.



① = Pyrite, ② = Clay, ③ = Organic pores, ④ = Quartz, ⑤ = Silicates, ⑥ = Calcite

Fig. 14. Minerals present in the coal shale sample.

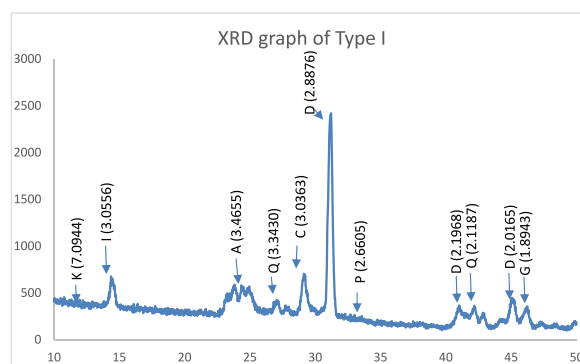


Fig. 15. XRD graph of type I.

4. Result

The tests were done for known fluoride solutions of initial concentrations of 3 ppm, 5 ppm, 7 ppm, and 9 ppm to know the preliminary effect on fluoride. A total of 320 standard water samples were prepared and tested for the total process. To decide the proper size of the adsorbent, different sizes (0.212 mm, 0.250 mm, 0.425 mm, and 0.600 mm) of shale were tasted for 3 ppm and 10 ppm solutions at a contact time of 30 min. It was observed that the adsorption efficiency is indirectly proportional to the size. Maximum

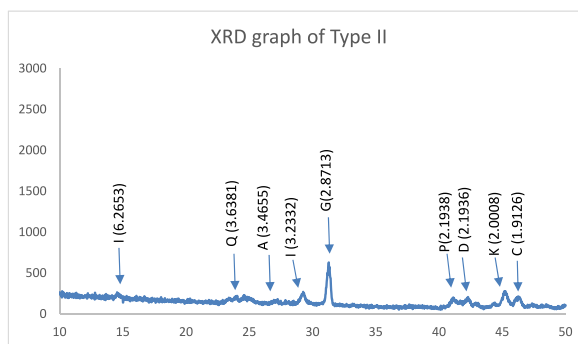


Fig. 16. XRD graph of type II.

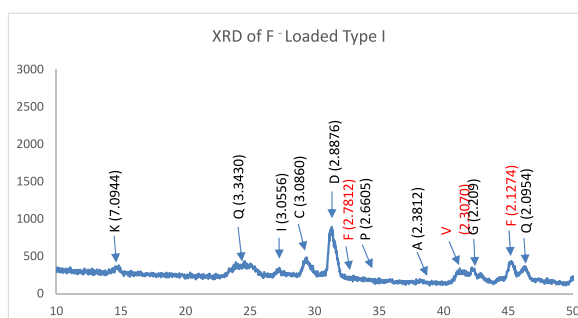
Fig. 17. XRD graph of F⁻ loaded type II.

Table 1

Mineral Phases obtained from XRD graph.

Sample	Mineral phases (%)										
	Kaolinite	Illite	Pyrite	Gypsum	Dolomite	Quartz	Calcite	Anatase	Villiaumite	Fluorite	
Type I	26.1	22.0	16.5	10.7	8.3	6.6	6.1	3.8	–	–	
Type II	20.9	23.7	17.8	11.5	8.2	7.2	6.6	4.1	–	–	
Type I + F- loaded	23.7	20.0	15.1	9.7	7.0	6.1	5.6	3.5	5.1	4.3	
Type II + F- loaded	19.9	22.6	17.0	11.0	7.8	6.8	6.3	3.9	–	4.8	

removal obtained in both cases was at 0.212 mm (Table 2). Lesser size adsorbents may have a greater surface area which helped in better adsorption onto the surface [14].

The effect on initial fluoride concentration was taken into consideration, using 0.212 mm old shale sample, the adsorption tests were done for 3 ppm, 5 ppm, 7 ppm and 9 ppm solution for 15 minutes. The result for all the cases indicated that maximum removal was obtained at 3 ppm initial solution as shown in Fig. 19. The minimum removal was obtained at a higher initial concentration, which may be due to the saturation of active sites of adsorbent at higher concentration due to the presence of more fluoride ions than the adsorption capacity.

To obtain the optimum dose of adsorbent, the adsorption was carried out by taking different doses such as 10 g/L-100 g/L of 0.212 mm old shale for 3 ppm initial fluoride solution at a contact time of 15 and 30 minutes. The result showed that 60 g/L is giving maximum removal but after it, there is no significant change in removal for 100 g/L (Fig. 20).

The adsorption test was conducted for different contact times 15 min, 30 min, 45 min, 60 min, and 24 h for fluoride removal using 0.212 mm old shale for 3 ppm initial fluoride solution. The result indicated that maximum removal is obtained in the first 1 h of

Table 2

Effect of shale size on adsorption.

Shale Size (IS 469/1972) (mm)	% Removal of Initial fluoride (3 ppm) for 30 min	% Removal of Initial fluoride (10 ppm) for 30 min
0.212	43	25
0.250	22	21.5
0.425	11	10
0.600	10.5	9.23

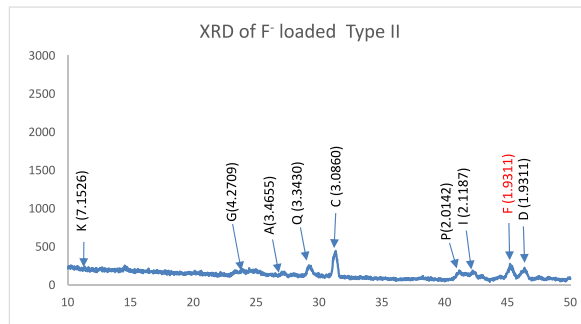


Fig. 18. XRD graph of F⁻ loaded type II.

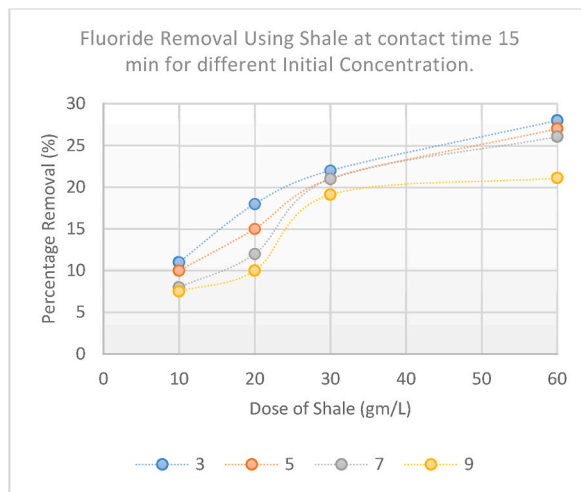


Fig. 19. Effect of initial concentration on adsorption.

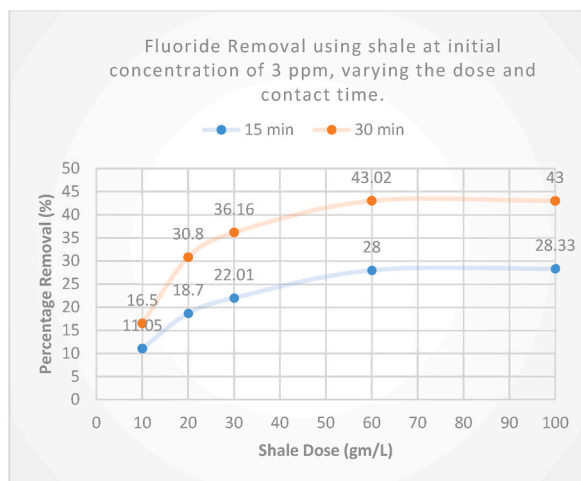


Fig. 20. Effect of Shale dose on Adsorption.

adsorption after which no significant change was obtained (Table 3).

The maximum removal of F⁻ was obtained at 60 min of contact time, to analyze the effect of different types of shale, a new shale sample of 0.212 mm was taken in water with 3 ppm initial fluoride solution for 60 min. The efficiency for Type II (fresh) shale was obtained at 40.02% compared to old shale at the same parameter giving an efficiency of 47.05% as shown in Fig. 21. Thus it can be

Table 3
Effect of contact time on adsorption.

Contact Time	% Removal
15 min	28
30 min	43
45 min	46.1
60 min	47.05
24 h.	47.19

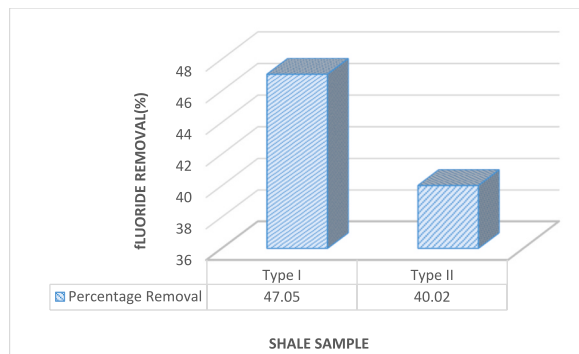


Fig. 21. Effect of shale type on adsorption.

observed that there is a significant change occurring in the shale sample when exposed to weathering action in long term.

The pH and present suspended solids play an important role in the quality of drinking water. The suspended solids should ideally be less than 1 NTU as per WHO standards. In the experiment, the pH and suspended solids were measured and the value obtained were within the desirable limit for suspended particle [15]. There is also a slight decrease in pH from the original pH of water. The pH for 3 ppm solution after a contact time of 24 h decreased from 4.52 to 4.1 and turbidity after defluoridation was obtained as 0.5 NTU. Hence the treated water has parameters within the permissible limit.

5. Kinetic of adsorption

Adsorption Kinetics is a measure of the adsorption uptake concerning the time at constant pressure or concentration, It is also used to measure the diffusion of adsorbate in the pores. Kinetic adsorption is a curve or line that describes the rate of retention or release of a solute from an aqueous environment to a solid phase interface at a given adsorbent dose, temperature, flow rate, and pH [16].

5.1. Pseudo-first-order model

The reactions that have higher order true rate law but are found to behave as first order are called pseudo first order reactions. This first-order model is used for the simplest adsorption process with very less contact time (20–30 min) also called the Lagergren pseudo-first-order kinetics, the model is described using a kinetic equation.

$$\ln(Q_E - Q_T) = \ln Q_E - k_1 T \tag{1}$$

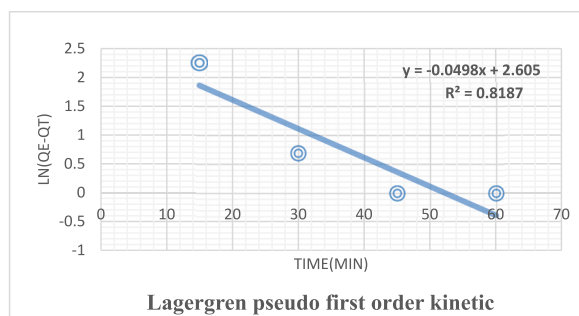


Fig. 22. Pseudo-first-order kinetic model (type I).

where, Q_E = the amounts of F^- ions adsorbed at equilibrium, Q_T = the amounts of F^- ions adsorbed at time T, K_1 = the adsorption rate constant.

The adsorption rate constant, k_1 (min^{-1}), was calculated from the plots of $\ln(q_e - q_t)$ versus time. From Fig. 22, we can observe that the model with K_1 value 0.0498, $R^2 = 0.8187$ value is very low to fit First order kinetics so this reaction may need a longer time to reach the eq-equilibrium. Similar to other types of shale with K_1 value 0.0518, $R^2 = 0.8203$ from Fig. 23.

5.2. Pseudo second order model

Second order kinetics describes that the reaction rate is proportional to the product of concentrations of two reactants in other words it is also based on assumption that the reaction is a one-step process. Here the rate-limiting step may be chemical adsorption or exchange of ions between two reactants.

The model is described using a kinetic equation.

$$T/Q_T = 1/K_2 Q_E^2 + t/Q_E \tag{2}$$

where, Q_E = the amounts of F^- ions adsorbed at equilibrium, Q_T = the amounts of F^- ions adsorbed at time T, K_2 = the adsorption rate constant.

The adsorption rate constant, K_2 (min^{-1}), was calculated from the intercepts and slope from plots of q_t/t versus time. Fig. 24 we can observe that the model with K_2 value 0.0327, R^2 0.9798 whereas for type II (Fig. 25), K_2 value 0.0236, R^2 0.6711. Type I adsorbent result in perfectly fit second order kinetics indicating that the rate-limiting step involves chemisorption phenomena, Type II is not fitting the model because of the low regression coefficient value.

5.3. The intra-particle diffusion model

This model is used to determine the occurrence of the intra-particle diffusion mechanism during the rate-controlling step of F^- ion adsorption. The model is represented by an equation

$$Q_T = K_i T^{0.5} + C_i \tag{3}$$

where, C_i = layer thickness, Q_T = the amounts of F^- ions adsorbed at time T, K_i = the diffusion rate constant.

From Fig. 26 we get the regression value 0.7335 and did not pass through the origin that is validating the intra-particle diffusion model. However, very high values of the intra-particle diffusion rate constant k_i ($8.9672 \text{ mg}/(\text{g}\cdot\text{min})^{0.5}$) and layer thickness C_i (25.139 mg/g) indicated that the step involving Intra particle diffusion might be the sole rate-limiting step. That indicates the adsorption depends on other parameters too, which may affect the rate of adsorption of the shale. But type II shale is following the diffusion model with a very high value of regression coefficient 0.9293 (Fig. 27).

6. Discussion

Performance comparison of shale with other such waste adsorbents can be difficult due to variations of parameters (pH, temperature, dose of adsorbent, contact time, initial fluoride solution etc.) and it is also dependant on the availability of material. In this paper adsorption of fluoride using a mine waste, viz. shale; has been studied in detail. Two types of shale were studied as fluoride adsorbents. Maximum equilibrium obtained for 3 ppm initial fluoride solution at contact time 60 min for adsorbent dose 60 gm/L for weathered shale. Kinetic of the reaction studies indicate that Type I (weathered) is following the pseudo second order kinetic model while; type II (fresh) adsorbent is following Intra particle diffusion model. This variation can be observed due to the internal changes that happened in the molecules due to weathering effect. The maximum removal efficiency was obtained for weathered shale at 47.05% in optimum conditions. Some other study regarding fluoride removal using waste has shown lesser removal efficiency than coal-weathered shales, such as Raw municipal solid waste (MSW) showed 42.6% [17], while MBS (Mahabir colliery shale) showed

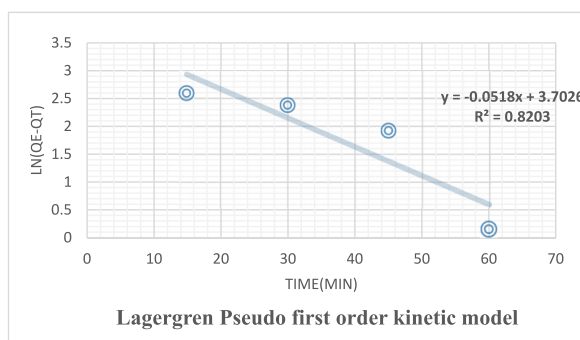


Fig. 23. Pseudo-first-order kinetic model (type II).

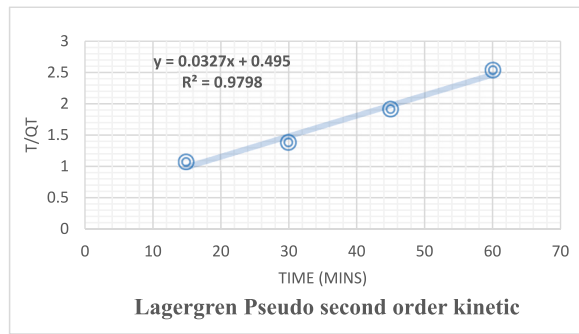


Fig. 24. Pseudo-second-order kinetic model (type I).

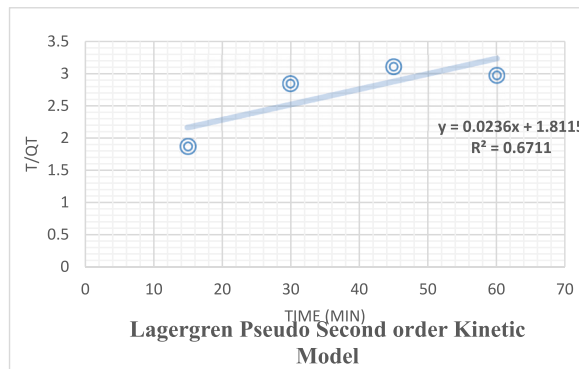


Fig. 25. Pseudo-second-order kinetic model (type II).

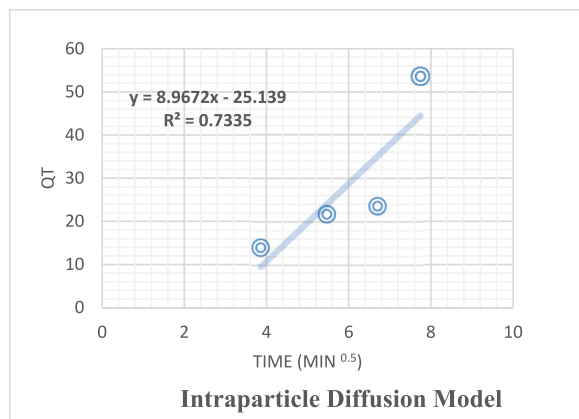


Fig. 26. Intraparticle diffusion model (type I).

46.4% [14] removal in its raw form. The long-term exposure to weathering action may have a significant effect on the pore structure, and organic content of shale particles. A deep study into the characterization of both shale, and pore structure analysis gave some explanation to the variant result in adsorption property as the weathered shale contains more clay, it has also more pores compared to the fresh shale.

Being so abundant as waste material in the mine industry shale can be used as an adsorbent for fluoride removal without affecting the quality of water in industrial applications.

6.1. Future scope

For further study Shale samples from different other mines such as Iron Copper, Bauxite, or Petroleum can be analyzed for fluoride

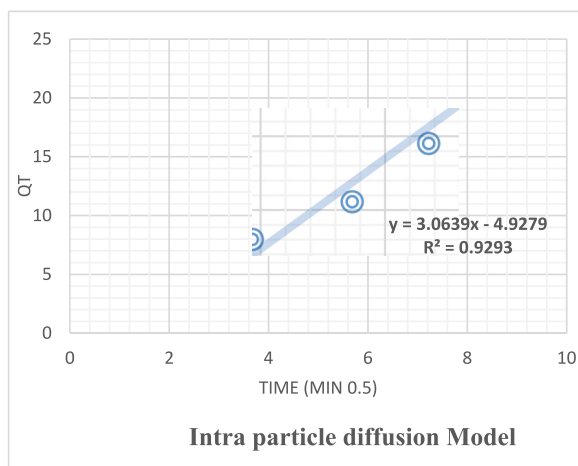


Fig. 27. Intraparticle diffusion model (type II).

removal. The effect of weathering can be studied more deeply to find out the changes in its mineralogy. Other ions apart from Fluoride can be used as parameters to be removed using this waste. So that the waste generated in tons can be reused properly.

6.2. Data availability

All data, models, and code generated or used during the study appear in the submitted article.

Author contribution statement

Bidyutprava Behera: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Himanshu Bhushan Sahu: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

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Data availability statement

No data was used for the research described in the article.

Declaration of interest's statement

The authors declare no competing interests.

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