Fluoride removal using shale: a mine waste

Manjari Kumari, Kalyan Adhikari, Susmita Dutta
National Institute of Technology, Durgapur, West Bengal, India
manjaridutt08@gmail.com

KEYWORDS
Shale, Fluoride, Heat activation, Kinetic Study, Equilibrium study

ABSTRACT:
In the present study, shale – a coal mine waste, has been used to remove fluoride from its aqueous solution. After collection, shale rocks were crushed, ground and sieved to desired size. Two forms of shale, such as native shale (NS) and heat activated shale (HAS) have been used for adsorption studies. Heat activation of shale has been done in a muffle furnace at three different temperatures viz., 350ºC, 450ºC and 550ºC for 1 h and the adsorbents have been designated as HAS350, HAS450 and HAS550 respectively. Native and heat activated shale have been characterized in terms of their specific gravity, organic carbon content, bulk density and moisture content. To test the efficiency of fluoride removal by different adsorbents, viz., NS, HAS350, HAS450 and HAS550, the adsorbents have been contacted with 10 mg/L fluoride solution individually at pH 3 for a contact time of 24 h. HAS550 showed the maximum fluoride removal efficiency of 88.8%. Effects of different experimental parameters like, pH, adsorbent dose and initial fluoride concentration on fluoride removal using HAS550 have been examined. A thorough kinetic study has been done by varying initial fluoride concentration and particle size in the range of 5-15 mg/L and 53-300μ respectively in a judicial manner. Kinetic and equilibrium data were found to fit best to pseudo-second order kinetic model and Freundlich isotherm model respectively.

1. INTRODUCTION

Fluorine is the lightest member of the halogen group and is one of the most reactive of all chemical elements. Fluorine in the environment is therefore found as fluorides which together represent about 0.06–0.09 per cent of the earth's crust (Fawell et al., 2006). The introduction of fluoride to surface or ground water may be from natural sources or anthropogenic sources. While dissolution of fluoride bearing rocks such as cryolite, fluorspar, hydroxylapatite, apatite etc., are the natural cause of fluoride contamination in ground water, the anthropogenic sources include effluents coming from different industries like superphosphate industry, aluminium and zinc smelters, brickworks, ceramic works, uranium enrichment facilities, coal fired power plants, oil refineries, etc (Jayapriya et al., 2011). Fluoride contamination in water can be considered as a double-edged sword (Sengupta and Thirumurthy, CPCB, India). Whilst ingestion of fluoride at a very low concentration (< 0.5 mg/L) may cause tooth decay, excessive consumption of fluoride (> 1.5 mg/L) for a long term may lead to skeletal damage, dental fluorosis, mental disorders in children, osteosclerosis and structural changes in DNA (Malakootian et al., 2011). According to World Health Organization (WHO) guidelines, the optimum concentration of fluoride in drinking water is 1.5 mg/L. The Bureau of Indian Standards, BIS (IS – 10500) has prescribed a desirable limit and permissible limit of fluoride in drinking water as 1.0 and 1.5 mg/L (Vardhan and Karthikeyan, 2011). Endemic fluorosis remains a challenging and extensively studied national health problem in India. The most seriously affected states are Andhra Pradesh, Punjab, Haryana, Rajasthan, Gujarat, Tamil Nadu and Uttar Pradesh (Fawell et al., 2006). The highest concentration observed to date in India is 48 mg/ l in Rewari District of Haryana (Fawell et al., 2006). Recent studies show that West Bengal, a state in India, is also not very far from severe fluoride contamination in ground water. Nine out of nineteen districts in West Bengal have fluoride levels in drinking water greater than permissible limits. Rural people are the main sufferer of fluoride contamination. Villagers who lived on fluoride contaminated water for most part of their lives have suffered serious consequences ranging from different extents of dental fluorosis to skeletal fluorosis (Sim and Leong, 2011). Thus, defluoridation of drinking water for removal of excess fluoride is mandatory for betterment of their lives. Though a number of studies have been made to develop

several processes to remediate fluoride from water, each process has its own difficulties and limitations. A cost-effective, environment friendly, technically viable process is in search. In the present study, shale – a sedimentary rock treated as coal mine waste in Raniganj area of West Bengal, has been used for adsorptive removal of fluoride from ground water to supply safe drinking water to the rural people of India.

Shale is obtained as mine waste during excavation of coal. It consists of different clay minerals like illite, kaolinite, quartz, chert, feldspar and smectite, which are responsible for adsorption characteristic of shale. It is found in abundance and free of cost, hence, its use for pollution control would serve both the purposes of water pollution remediation as well as solid waste management. As far as known, no work on removal of fluoride using shale has been reported. Here lies the novelty of the present work.

2. MATERIALS AND METHODS

All the experiments were done in triplets and the average values have been reported. Reagents used were of analytical grade obtained from MERCK, India.

2.1. Collection and preparation of adsorbent

Shale, a coal mine waste was obtained from Mahabir Colliery in Raniganj Coalfield of West Bengal, India (Latitude: 23º37'05" & Longitude: 87º06'19")**.** Shale rocks were first broken down to small pieces using a hammer and later crushed in a jaw crusher. It was then ground to powdered form in a ball mill. The powdered shale was sieved to get desired particle size. Two forms of shale were used for adsorption studies, native shale (NS) and heat activated shale (HAS). Heat activation of shale was done in a pre-heated muffle furnace at 350ºC, 450ºC and 550ºC separately taken in heat-resistant crucibles for 1 h. The adsorbents, thus prepared, were designated as HAS350, HAS450 and HAS550 respectively.

2.2. Characterization of adsorbent

Specific gravity, bulk density, total organic carbon and moisture content of NS, HAS350, HAS450 and HAS550 were determined using standard methods. Surface area of the adsorbents was determined by BET surface area analyzer (BET-QUANTOCHROME MAKE NOVA 4000E, USA). To get topographical characterization and the effect of fluoride binding on surface, SEM analysis was done with original and fluoride loaded adsorbent using JEISS EVO 18, GERMANY.

2.3. Fluoride removal

2.3.1. Selection of adsorbent and Effect of different parameters on fluoride removal

Fluoride stock solution (1000 mg/L) was prepared by dissolving 2.211 g of NaF powder in 1L de-ionized water. Subsequent concentrations of fluoride for experimentation were prepared by dilution of this stock solution. Volume of solution taken for each run was fixed at 50 ml. pH of solution was adjusted using 0.1M HCl and 0.1M NaOH solution. Removal of fluoride was studied by contacting requisite amount of adsorbent with the fluoride solution at desired pH in a batch contactor for 24 h. The resulting slurry was then centrifuged at 7000 rpm for 20 min. Residual fluoride concentration of the resulting solution was determined using Ion-selective fluoride electrode (Ionmeter 4 STAR, B 36531, Thermoscientific). To compare the fluoride removal efficiencies of NS, HAS350, HAS450 and HAS550, 3.5g adsorbent was contacted with 10 mg/L fluoride solution at pH 3 for 24 h. From the analysis, it was seen that HAS550 showed the maximum fluoride removal efficiency of 88.8% in comparison with other adsorbents like NS, HAS350 and HAS550. Therefore, further studies were performed using HAS550 only. Effect of different experimental conditions on fluoride removal viz., initial pH of solution (2-8), initial fluoride concentration (2.5-15 mg/L), adsorbent dose (0.5-4.5 g/50 ml) and size of adsorbent particle (53-300µ) were examined with HAS550. In order to keep the cost of operation minimum, temperature was not considered a parameter, so, all experiments were done at ambient temperature of 35°C.

2.3.2. Kinetic study

Kinetic study was carried out to examine the performance of adsorbent with time and to understand the nature of adsorption. Initial fluoride concentration (5-15 mg/L) was selected as a parameter to be studied. Kinetic study varying the initial fluoride concentration was done with 3.5g adsorbent dose at pH 3 and particle size of 90µ. Experiments were performed for 24 hours and after every 2h, samples were collected and analyzed for residual fluoride concentration.

2.3.3. ***Equilibrium study***

In any adsorption process, the distribution of adsorbate between the liquid and solid phase finally attains equilibrium and hence the concentration of adsorbate in solution becomes constant. Equilibrium study was done. The nature of adsorption of the adsorbate on the adsorbent can be predicted using adsorption isotherm models. In the present study, adsorption equilibrium data were fitted to two isotherm models, Langmuir and Freundlich. Langmuir adsorption isotherm model assumes that the nature of adsorption on the adsorbent is homogeneous, i.e. all the adsorbent sites are equivalent and the adsorbate forms a monolayer on the surface of adsorbent. While Freundlich adsorption isotherm model assumes that adsorption occurs on a heterogeneous surface and forms multi-layers on the adsorbent surface (Gao et al., 2009). Equilibrium study was done by varying the initial fluoride concentration from 5-30 mg/L keeping other parameters like adsorbent dose, intial pH of solution, size of particle and contact time constant at 3.5 mg, 3, 90µ and 24 h respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of adsorbent

Specific gravity, bulk density, moisture content and total organic carbon of NS, HAS350, HAS450 and HAS550 have been determined and presented in Table 1. Specific gravity is more for heat activated shale than its native form. It increases with activation temperature also. The least is obtained for NS whereas highest value is obtained for HAS550. Bulk density has been found to be almost constant. As expected, moisture content decreases with heat activation temperature and lowest is obtained for HAS550. BET surface area has been determined to be 11.02 and 20.08 m^2/g for NS and HAS550 respectively. This increase in surface area is attributed to loss of different volatile materials and water of crystallization upon heat activation. SEM images of NS, HAS550 and fluoride loaded HAS550 are shown in Figure 1-3. Sharp edges are observed in Figure 1, whereas, for the same magnification HAS550 shows blunt shaped particles after heat activation (Figure 2). HAS550 becomes fluffy and bulky which results in increase of surface area as well as adsorption capacity. Particle surface becomes covered with fluoride after adsorption as seen in Fig. 3.

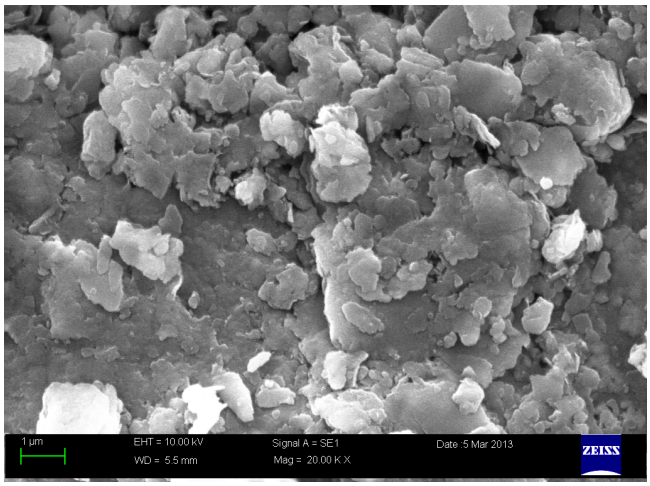

Figure 1. SEM photograph of NS

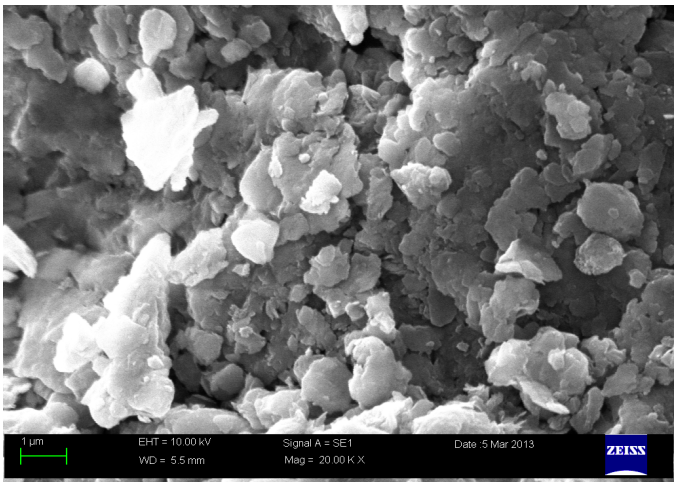

Figure 2. SEM photograph of HAS550

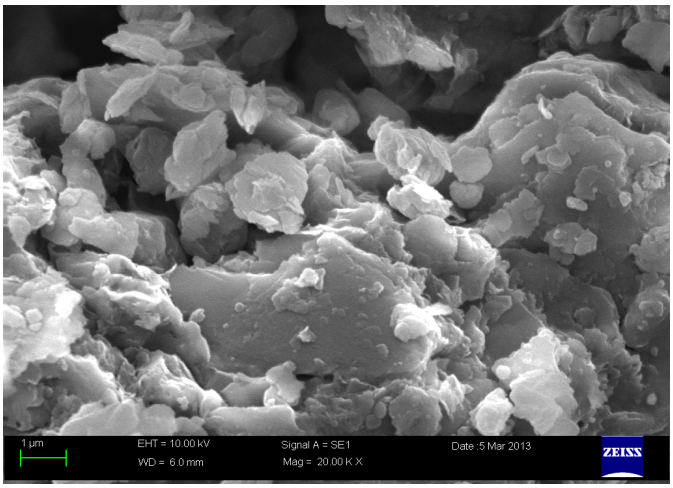

Figure 3. SEM photograph of Fluoride loaded HAS550

Table 1. Physical characteristics of NS, HAS350, HAS450 and HAS550

Adsorbents	specific gravity	bulk density (g/cc)	moisture content (%)	Total organic carbon (%)
NS	2.1507	0.7633	2.1793	1.0702
HAS350	2.3906	0.8333	0.1001	5.0637
HAS450	2.3908	0.8333	0.0199	4.7778
HAS550	2.4692	0.7633	0.0099	2.4093

3.2. Selection of adsorbent and effect of different experimental parameters

During comparative study, HAS550 shows the maximum fluoride removal of 88.8% while HAS350 and HAS450 show removal of 70.01% and 78.49% respectively under identical condition as seen in Figure 4. Native shale shows lowest removal of 44% at same condition. Since HAS550 has been found to be most efficient, it has been selected for batch adsorption studies.

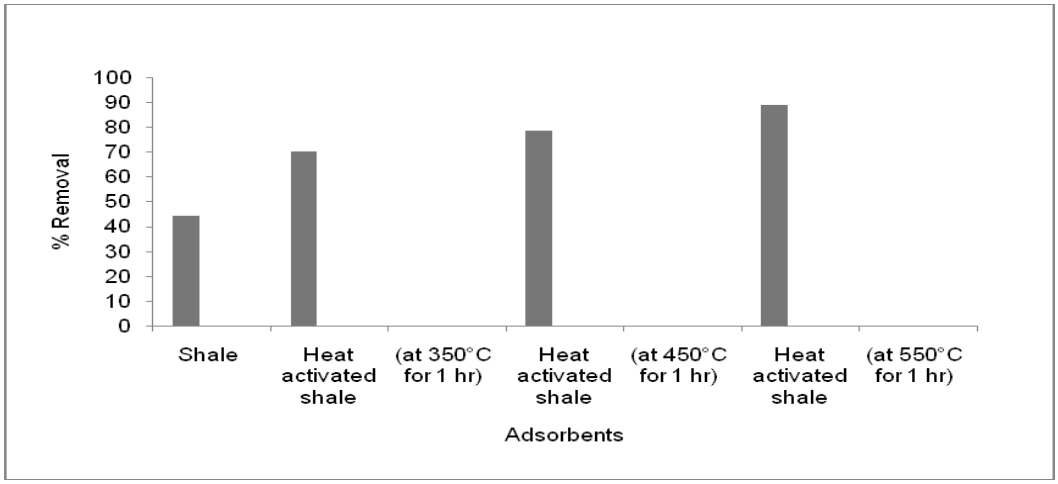

Figure 4. %Removal of fluoride by native and different heat treated shale

Effect of pH on adsorption of fluoride onto HAS550 has been seen by varying it from 2 to 8. Maximum removal of 88.72% has been recorded at an initial pH 2 when initial fluoride concentration and adsorbent dose have been kept constant at 10 mg/L and 3.5g respectively in a contact time of 24 h. From Figure 5, it is seen that when pH increases from 2 to 8, removal of fluoride decreases from 88.72% to 37.76%. This may be attributed to the accumulation of negative charge over the surface at high pH which repels fluoride ion leading to less removal. On the other hand, removal was seen to increase monotonously as pH decreases. This may be due to the accumulation of positive ions (mainly H^+) on adsorbent at lower pH values for which fluoride readily gets adsorbed on the surface. Similar results have been reported by other scientists as well (Gao et al., 2009; Wambu et al., 2012; Babaeivelni and Khodadoust, 2012). Furthermore, it has been observed that the pH of the treated water automatically reached to around 5.5 from an initial value of 3. This indicates the probable usage of treated water for safe consumption. So treatment of drinking water at an acidic pH with heat activated shale is not a major issue.

Fluoride removal efficiency of HAS550 has been seen to increase with increase in adsorbent dose. Removal increased from 38.1% to 89.3% with increase in adsorbent dose from 0.5g to 4.5g as shown in Figure 6. After 3.5g of adsorbent dose, the removal becomes independent of it. Thus, 3.5g was chosen to be the optimum adsorbent dose. The increase in removal with increase in adsorbent dose is attributed to the increase in adsorbent sites available for the same amount of fluoride anions. Initial fluoride concentration has been varied from 2.5 mg/L to 15 mg/L as shown in Figure 7. Maximum removal of 95.46% has been seen at initial fluoride concentration of 2.5 mg/L. This value decreases to 83.70% at an initial fluoride concentration of 15 mg/L. Decrease in removal efficiency with increase of initial fluoride concentration is mainly due to more competition of fluoride ions for the same number of available adsorption sites.

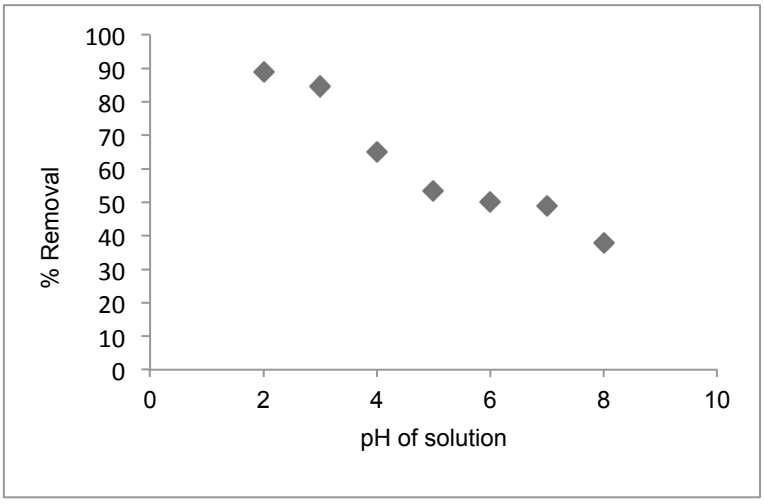

Figure 5. Effect of initial pH of solution on fluoride removal

Effect of variation of size of particle on fluoride removal has been seen by varying it from 53µ to 300µ. Removal has been found to be inversely proportional to the size of particle. It increases as size of particle decreases being, maximum at 53µ as shown in Figure 8. Although removal increases with decrease in size of particle, this increase is not as significant as observed in case of other experimental parameters. HAS550 shows removal of 91.9% at particle size of 53µ and 87% at particle size of 300µ. Since the increase is not very significant, an optimum value of 90µ has been selected for further experimentation.

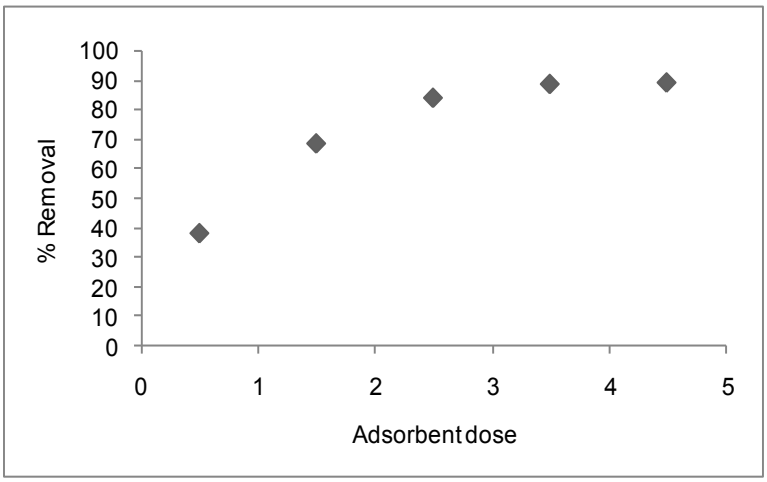

Figure 6. Effect of adsorbent dose on fluoride removal

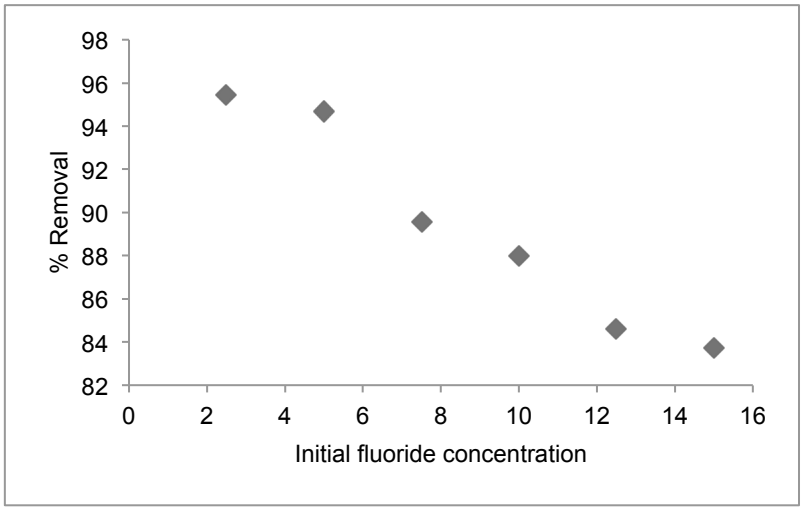

Figure 7. Effect of initial fluoride concentration on fluoride removal

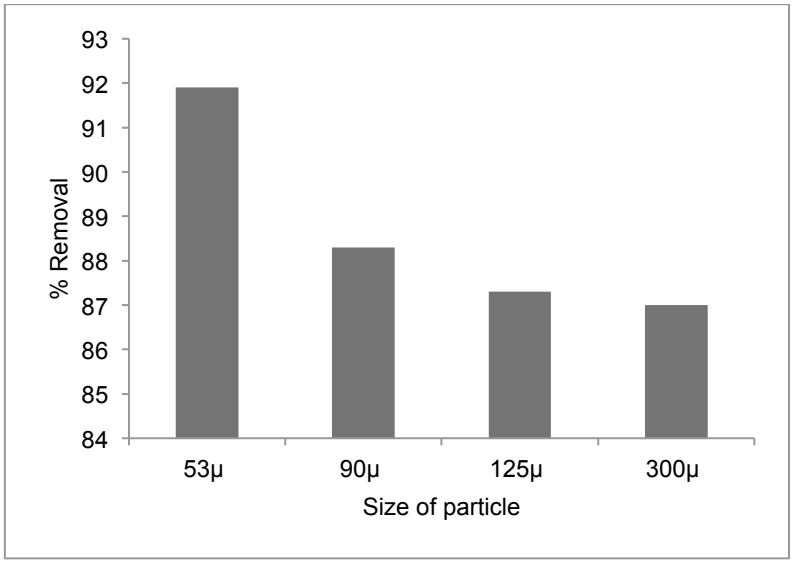

Figure 8. Effect of adsorbent particle size on fluoride removal

3.3. Kinetic study

Kinetic study has been done at different initial fluoride concentrations in the range of 5-15 mg/L. The variation of %removal with time considering initial fluoride concentration as a parameter is shown in Figure 9. It has been observed that, with increase in initial fluoride concentration, the %removal decreases. It has also been seen that, after 20 h of contact time, there is negligible increase in removal of fluoride and the solution attains equilibrium. Kinetic data have been fitted to Lagergren pseudo-first order model, pseudo-second order model and Morris-Weber intra-particle diffusion model (Svilovic et al., 2010) separately and the values of parameters are shown in Table 2. Pseudo-second order kinetic model has been found to fit best as evidenced from the values of Correlation coefficients.

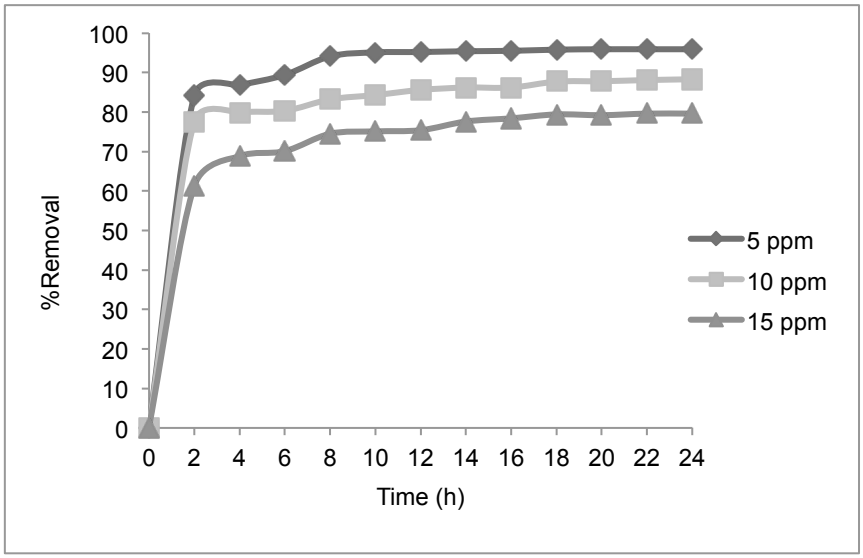

Figure 9. Kinetic study at different initial fluoride concentration

Table 2. Various kinetic parameters of the kinetic models

Initial fluoride concentration (mg/L)	Pseuod-first order model $(\log(q_e - q_t) = \log q_e - k_1 t)$			Pseudo-second order model $\frac{t}{q_t} \quad \frac{1}{(k_2)(q_e^2)} + \frac{t}{q_e}$			Intra-particle diffusion model $(q_t = k_p t^{1/2})$	
	k_1	Q	R^2	k_2	q_e	R^2	k_p	R^2
5	-0.256	0.037	0.944	0.046	7,143	0.998	23.22	0.878
10	-0.073	0.845	0.936	0.399	2.326	0.985	8.234	0.966
15	-0.099	1.256	0.902	0.429	1.616	0.996	6.231	0.900

3.4. Equilibrium study

Equilibrium study has been done to determine the adsorption capacity of the adsorbent. Equilibrium data has been fitted to linearized forms of Langmuir and Freundlich adsorption isotherms and the values are shown in Table 3. As is evident from the data, the obtained adsorption equilibrium data fits to Freundlich adsorption isotherm better than Langmuir adsorption isotherm. It indicates that the surface of the adsorbent is heterogeneous and the adsorbate forms multi-layer on the adsorbent surface.

Table 3. Adsorption isotherm parameters of fluoride adsorption on HAS550

Langmuir $\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e}$	Freundlich $\log q_e = \log K_F + \frac{1}{n} \log C_e$
R^2 = 0.962 q_m = 0.358 K_L = 0.320	R^2 = 0.994 1/n = 1.631 K_F = 0.0843

4. CONCLUSION

Heat Activated Shale has been proved to be a promising adsorbent for fluoride remediation from its aqueous solution. Maximum removal of 95.46% was observed for an initial fluoride concentration of 2.5 mg/L at an adsorbent dose of 3.5g at pH 3 and contact time of 24 h. Since pH value reaches near to neutral after treatment with HAS550, fluoride removal at acidic conditions is not an issue. Fluoride adsorption data has been found to fit best to Freundlich adsorption isotherm indicating multilayer adsorption on a heterogeneous surface. The reaction follows pseudo-second order kinetics. Adsorption capacity has been found to be 0.358 mg/g. Shale is generated as mine waste, so fluoride removing using shale serves both the purpose of solid waste management as well as pollution abatement. However, this is a preliminary study and a more elaborate study encompassing the search of root causes for fluoride adsorption on shale and detailed parametric study with real fluoride contaminated ground water is required.

5. REFERENCES

Babaeivelni, K. and Khodadoust, A.P. (2012): Adsorption of fluoride onto crystalline titanium dioxide: Effect of pH, ionic strength and co-existing ions, Journal of Colloid and Interface Science, S0021-9797(12), pp. 1351-1353.

Fawell, J.; Bailey, K.; Chilton, J.; Dahi, E.; Fewtrell, L.; Magara, Y. (2006): Fluoride in drinking water, World Health Organization, 2006, pp. 107-127.

Gao, S.; Cui, J.; Zhenggui, W. (2009): Study on the fluoride adsorption of various apatite materials in aqueous solution, Journal of Fluorine Chemistry 130 (2009), pp. 1035-1041.

Jayapriya, G.; Ramya, R.; Rathinam, X.R.;Sudha, P.N. (2011): Equilibrium and kinetic studies of fluoride adsorption by chitin/cellulose composite, Archives of Applied Science Research, 2011.

Kagne, S.; Jagtap, S.; Dhawade, P.; Kamble, S.P.; Devotta, S., and Rayalu, S.S. (2008): Hydrated cement: A promising adsorbent for the removal of fluoride from aqueous solution, Journal of Hazardous Materials 154 pp. 88–95.

Malakootian, N.; Moosazadeh, M.;Yousefi, N.; Fatehizadeh, A.(2011): Fluoride removal from aqueous solution by pumice: case study on Kuhbonan water, African Journal on Environmental Science and Technology Vol. 5(4).

Paikaray, S. Banerjee, S. Mukherji, S. (2005): Sorption behavior of heavy metal pollutants onto shales and correlation with shale geochemistry, Environmental Geology,47, pp. 1162–1170.

Paikaray, S. Banerjee, S. Mukherji, S. (2005): Sorption of arsenic onto Vindhyan shales: Role of Pyrite and Organic Carbon. Current Science, 88, pp.10.

Sengupta, B.; Thirumurthy, S.G.: Status of water treatment plants in India, Central Pollution Control Board, India.

Sim, J.M.; Leong, K. M. (2011): Feasibility study on fluoride removal in drinking water in Mehsana, India, International NGO Journal, pp. 1-4.

Svilovic, S.; Rusic, D.; Basic, A. (2010): Investigations of different kinetic models of copper ions sorption on zeolite 13X, Desalination (259), pp. 71–75.

Vardhan, C.M.V. & Karthikeyan, J. (2011): Removal of fluoride from water using low-cost materials, Proceedings of Fifteenth International Water Technology Conference.

Wambu, E.W.; Onindo, C.O.; Ambusso, W.J. & Muthakia, G.K. (2012): Fluoride adsorption onto an acidic treated lateritic mineral from Kenya: Equilibrium studies, African Journal of Environmental Science and Technology Vol. 6(3), pp. 160-169.