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KINETICS, ISOTHERM AND THERMODYNAMICS STUDIES OF FLUORIDE UPTAKE BY POLYANILINE WITH DOPED CHLORIDE

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ABSTRACT

Fluoride though has essential benefits for health, excessive fluoride concentration in water leads to several health issues including mottling of teeth and bones etc. This study explores to study the feasibility of fluoride uptake by adsorbent polyaniline doped with chloride and identifies the adsorption parameters including adsorption kinetics, isotherm and thermodynamics. For this purpose, adsorption experiments were conducted at a various initial concentrations of fluoride, dose of adsorbents and various temperatures. Rapid adsorption during the first 5 minutes yields more than 80% uptake of fluoride on PANI-Cl-jute and reached the adsorption equilibrium within 120 minutes suggesting predominant chemical adsorption nature. With increase in initial $F^{\square}$ *concentration,* $F^{\square}$ *uptake increases from 0.5 – 12.5 mg/g. With varying adsorption temperature from 293 to 313 K reveals a decrease in* $F^{\square}$ *uptake from 40% to 19%. The addition of heat inhibits the adsorption process revealing that the adsorption itself emits heat and thus is an exothermic reaction. Also, thermodynamics study reveals a spontaneous reaction between PANI-Cl-jute and* $F^{\square}$ *below 273 K and also no significant change in the internal structures of the adsorbent PANI-Cl-jute during the adsorption process. During the study on the effect of PANI-Cl-jute dose, an increase in dose from 2 – 20 g results in an increase in* F^{-} *removal (%) from 30 - 48% and 10% - 27% respectively for initial concentrations 10 mg/L and 20 mg/L. However,* $F^{\square}$ *removal slowed down after a dose of 15 g/L due to attainment of equilibrium between* $F^{\square}$ *and PANI-Cl-jute at a particular operating condition. Analysis of adsorption isotherm was conducted through Langmuir and Freundlich isotherm. The data were treated using both the non-linear and linear equation of the isotherms and showed favourable adsorption of* $F^{\square}$*. Desorption studies with a strong base could recover the adsorbed* $F^{\square}$ *by 80-90% and the adsorbent could be reused until the 7th cycle effectively and thus increase its* $F^{\square}$ *uptake capacity.*

Keywords*: Adsorption; pseudo-second-order; polyaniline; Langmuir isotherm; Freundlich isotherm; desorption.*

1. INTRODUCTION

It is already well known that the presence of fluoride in excess above the permissible limit has serious effects on health and precisely on skeletal tissue, bones and teeth. The difference in effects of fluoride unlike other ions is that even a deficiency of fluoride content in the water results in tooth decay and dental carries also. On the other hand, consumption of a higher dose of fluoride causes various effects such as skeletal fluorosis and molting of teeth, brain damage, cancer, Alzheimer's syndrome and thyroid disorder [1,2]. Thus WHO set its permissible limit at 1.5 mg/L. Anthropogenic releases of fluoride contaminated water include industries from ceramic production, semi-conductors manufacturing, electroplating, fertilizer and coal and power stations [3]. Several techniques are employed for its effective removal and some widely practices techniques are adsorption [4], ion exchange, precipitation [5], electrolysis [6] etc. Nanofiltration is one of the most recently explored methods [7]. With an emphasis on the cost of operation, adsorption is reported to be very effective along with its flexibility in the process [4]. Several low-cost adsorbents based on activated carbons, biosorbents [8] are reported and the focus towards more effectiveness with respect to adsorption time also leads to the application of modified metal oxide and polymeric material [9], polymeric adsorbent like polyaniline (PANI) [10], etc. To attain a stable inert adsorbent, support materials are also used during polymer adsorbent syntheses like alumina [11] and tamarind seed [12]. Therefore in search of a better adsorbent for the effective uptake of fluoride, this study focus on the employment of adsorbent polyaniline polymer synthesized with chain inhibitor paraphenylenediamine with doped chloride on the surface of jute fiber as supporting material (PANI-Cl-jute) and investigated for adsorption of fluoride. The main objectives of this study are the identification of adsorption kinetic, best fit isotherm, temperature effect and desorption of the adsorbed ions.

2. MATERIALS AND METHODS

2.1 Materials

AR grade from Merck chemicals was purchased and used as received. The presence of impurities in aniline was filtered through distillation using KOH. Merck (AR Grade) and used as received. All the samples were prepared using double distilled water (DURA Series Analytical Technologies Ltd.) and a Fluoride stock solution of 100 mg/L was prepared daily. Further, lower concentrations of F^{-} for experiments were prepared by series dilution of the stock solution. All the experiments and estimation were done in plastic wares avoiding glassware to minimize the adsorption of fluoride in the glass.

2.2 Methods

The synthesis of polyaniline was carried out by mixing 21.5 mmol aniline ($C_6H_5NH_2$) and 3.05 mmol ammonium peroxydisulfate [$(NH_4)_2S_2O_8$] at 0– 5 ^{0}C. Various concentration of HCl (0.1, 0.5, 1, 1.5 and 2 M) was added at different sets of polymer preparation for doping chloride followed by the addition of 5 g jute as a support medium. The aniline is oxidized to obtain a polymer with the introduction of chain terminator agent para-phenylenediamine and kept overnight to complete the reaction. An alkali treatment (1 M NH_4OH) was given to ensure complete deprotonation and the obtained adsorbent is dried and used as an adsorbent (PANI-Cl-jute). Fluorides concentrations were estimated using Ion selectivity electrode (Orion Star A211 Thermo Fisher) using TISAB buffer.

2.3 Adsorption Experiment

The batch experiment for adsorption was conducted using a 500 mL solution spiked with a known concentration of F^- in a 1000 mL beaker. Pre-determined adsorbent PANI-Cl-jute was contacted with the solution and maintained homogeneity using a rotatory shaker at approximately 300 rpm. All the adsorption experiments were conducted at pH 1 whose initial investigation was reported in our previous work[13]. The amount of F^- adsorption per unit weight of adsorbent at time t, q_t (mg F^-/g), was calculated using the following equation:

$$q_t = \frac{(C_0 - C_e)}{M} V \tag{1}$$

where C_o is the initial fluoride concentration (mg/L); C_t is the fluoride concentration at time t (mg/L); V is the solution volume (L) and M is the adsorbent mass (g). When adsorption reached its equilibrium, q_t becomes q_e and C_t becomes C_e.

3. RESULTS AND DISCUSSION

3.1 Initial concentration effects and adsorption kinetics

The effect of Initial F^- concentration of adsorption was studied by conducting experiments with varied initial F^- of 5, 10 and 20 mg/L contacting with 2 g/L PANI-Cl-jute. As represented in Fig. 1, the adsorption equilibrium time of F^- on PANI-Cl-jute was well within 120 minutes for all varied concentrations of 5-20 mg/L suggesting rapid adsorption. During the first 5 minutes of adsorption, more than 80% F^- were adsorbed indicating the predominant chemical adsorption of F^- on PANI-Cl-jute. With an increase in F^- concentration from 5 to 20 mg/L, the amounts of ions adsorbed (q_t) increase from 0.5 to 12.5 mg/g. This phenomenon is due to the availability of more F^- ions to adsorbed at higher F^- concentration whereas adsorption at lower F^- concentrations tends to have unsaturated PANI-Cl-jute thereby having lower q_t values. The data were analyzed using Pseudo Lagergren's first and second-order reaction[14] model eq and kinetics were identified. (2 & 3).

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{2}$$

$$q_t = q_e \frac{q_e k_2 t}{1 + q_e k_2 t} \tag{3}$$

where q_e and q_t are the amount of adsorbate adsorbed at equilibrium and at a time 't' respectively per unit weight of adsorbent. k_1 and k_2 are 1st and 2nd order rate constant respectively. The kinetics equation can be further linearised as

$$log(q_e - q_t) = log\ \ q_e - \frac{k_1}{2.303} t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{5}$$

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The kinetics data were fed on the first and second-order equation and all the coefficients of the kinetics are presented in Table 1. The experimental and predicted q_e values were also compared through evaluated errors using the Chi-square equation (Eq. no. 6) of the kinetic models.

$$\lambda^2 = \sum_{n=0}^{n} \frac{(q_{\exp} - q_{pre})^2}{q_{\exp}} \tag{6}$$

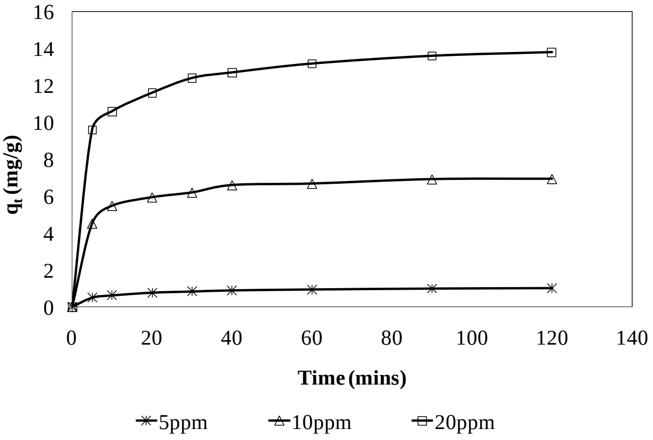

Fig. 1 Effect of initial F^- concentration on adsorption

Table 1 Kinetic parameters for F^- adsorption on PANI-Cl-jute

Co	Slope	Intercept	R^2	k	Experimental (q_e)	Predicted (q_e)	λ^2
5	-0.059	-0.14	0.945	0.059	1.03	0.87	0.368
10	-0.055	-0.041	0.947	0.055	1.74	0.96	4.255
20	-0.040	0.433	0.918	0.040	3.45	1.54	10.797
5	0.923	7.017	0.999	0.161	1.03	1.01	0.011
10	0.559	2.001	0.999	0.156	1.74	1.79	0.011
20	0.282	1.067	0.999	0.074	3.45	3.55	0.067

From Table 1, it's evident that the correlation coefficient (R^2) value for 1st order equations was below 0.95 for experiments with initial F^- of 5, 10 and 20 mg/L suggesting the inability of the adsorption data to fix on the kinetic equation. On the contrary, R^2 value for 2nd order is well above 0.99 and λ^2 value is less than 0.01. It's very comprehensible from these observations that the adsorption of F^{-} on PANI-Cl-jute follows Lagergren's 2nd order kinetic model. Similar second-order kinetics data fixing of fluoride adsorption are also reported on polymer[13,15], amine rich adsorbent chitosan[9,16,17]. The second-order kinetics implies that chemical adsorption involving valent forces through sharing or exchange of electrons between the adsorbent and adsorbate is the rate-limiting step[10]. With initial F^{-} concentration increase from 5 – 20 mg/L, the pattern of rate kinetics for 2nd order (k_2) value decrease from 0.161 – 0.074 mg.g/min and the trend is also similar to that of monetite bundles inlaid in chitosan with k value, 0.410 – 0.075 mg.g/min[19].

3.2 Temperature Effect

The effects of temperature on F^{-} adsorption was examined by conducting experiments with F^{-} 10 mg/L and PANI-Cl-jute 2 g/L and at a varying temperature from 293 to 313 K. The removals (%) were observed (Fig. 2) to decrease from 40% to 19% with the increase in temperature. To further study the thermodynamics of the adsorption, using Vant Hoff's equation was used and the plot of 1/T Vs Ln K_d is plotted in Fig. 3[18,19]. The thermodynamic parameters are evaluated as ΔH: -38.851 KJmol^{-1}, ΔS: -141Jmol^{-1}K^{-1} and ΔG: 2.74. The positive slope of 4673 (Fig. 3) indicates the exothermic process of the extraction process and the energy released because the total energy of the products is less than that of the total energy of the reactants. The negative ΔS suggests that the products have lower entropy than the reactants, which is not spontaneous by itself and the adsorption process involves an associative mechanism and reflects that no significant change occurs in the internal structures of the adsorbent PANI-Cl-jute during the adsorption process[20]. Again, both terms ΔS and ΔH are negative suggesting that the Gibbs free energy equation is balanced and temperature-dependent. The temperature at which ΔG = zero is evaluated as 273 K and therefore below 273 K, the reaction will be spontaneous. On the contrary, polyaniline doped chloride synthesized without paraphenylenediamine as a chain-terminating (PANI-Cl-jute) agent showed endothermic behavior of F^{-} adsorption[21]. The probable reason is the difference in mechanism of binding through ion exchange of F^{-} and doped chloride only against an additional binding mechanism for PANI-Cl-jute through electrostatic attraction at the terminal end of the polymer.

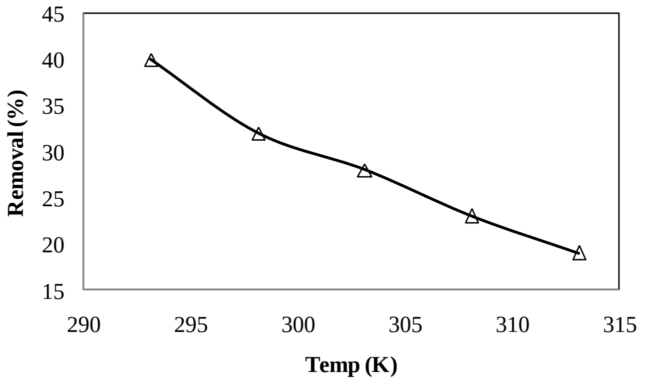

Fig. 2 Effect of temperature on adsorption of F^- on PANI-Cl-jute

3.3 Dose Effect and adsorption isotherm

The effect of adsorbent dose on adsorption of F^- was studied by varying PANI-Cl-jute doses of 2, 4, 6, 8, 10, 15 and 20 g contacted with initial F^{-} of 10 mg/L and 20 mg/L (Fig. 4). As the adsorbent dose increased from 2 – 20 g, F^{-} removal (%) for initial concentrations 10 mg/L and 20 mg/L increased from 30 - 48% and 10% - 27% respectively. The increase in adsorbent dose yields more active sites to adsorbed resulting in higher uptake of fluoride. However, after a rapid increase in F^{-} adsorption till PANI-Cl-jute dose up to 15 g/L, F^{-} removal slowed down and attained an asymptotic value for higher PANI-Cl-jute dosage. This can be explained as the attainment of equilibrium between F^{-} and PANI-Cl-jute at a particular operating condition and the effect had been termed as ''solid concentration-effect'' i.e. overcrowding of particles[22]. On the other hand, q_e decreased from 0.80 to 0.22 mg/g and 1.50 to 0.25 mg/g for initial F^- 10 mg/L and 20 mg/L respectively despite the increase in the dose of PANI-Cl-jute. At the higher dose of the adsorbent, several active adsorbent sites are left unutilized but which are accounted for q_e value and hence the decrease in q_e value.

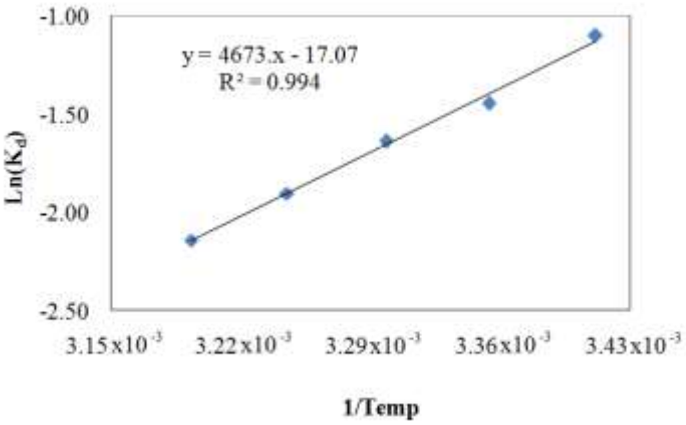

Fig. 3: 1/T Vs K_d

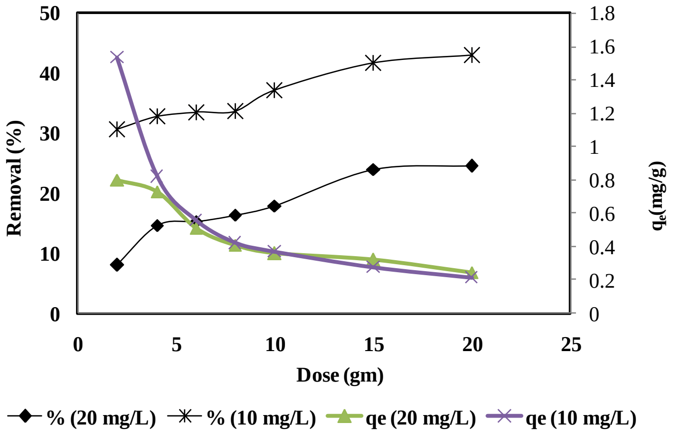

Fig. 4: Effect PANI-Cl-jute dose on F^- uptake

The adsorption isotherm is the functional relationship between the amounts of ions adsorbed onto the adsorbent and the ions left in the bulk solution. This relation can be explained by several isotherms and the most widely applied models are Langmuir[23] and Freundlich's isotherm[7].

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \tag{7}$$

$$q_e = K_f C_e^{1/n} \tag{8}$$

Their respective linearized expressions are represented as

$$\frac{1}{q_e} = \frac{1}{q_{max} b C_e} + \frac{1}{q_{max}} \tag{9}$$

$$Log(q_e) = Log(K_f) + nLog(C_e) \tag{10}$$

where C_e and q_e are equilibrium concentration of ions (fluoride) at liquid phase and solid phase respectively; q_{max} and ‘b’ are Langmuir’s maximum monolayer coverage (mg/g) and adsorption energy-related constant (L/mg); K_f is Freundlich’s bonding energy constant $[(mg/g)(L/g)^{1/n}]$ and ‘n’ varies with the heterogeneity of adsorbent and for favourable adsorption process. Therefore to identify the appropriate isotherm, adsorption experiments were conducted with initial F□ concentration of 1, 2, 3, 4, 5, 7, 10, 13, 15, 18 and 20 mg/L, contacted with 10 g/L PANI-Cl-jute and the data were treated with both the Linear and nonlinear equations of Langmuir and Freundlich isotherm. Employing the Langmuir linear equation for the plot of $1/C_e$ Vs $1/q_e$ and Log C_e Vs Log q_e for Freundlich, isotherm coefficients are evaluated and shown in Table 2. The nonlinear isotherms are also fixed using SigmaPlots 10.0 and the corresponding coefficients are also incorporated in Table 2. The correlation coefficient (R^2) of linear and nonlinear for both Langmuir and Freundlich are higher than 0.95 suggesting the conformity of both the isotherms onto adsorption of F□ on PANI-Cl-jute. However, higher R^2 (more than 0.98) and lower λ^2 (less than 0.1) for Langmuir suggest a better fit for Langmuir isotherm than that of Freundlich. Comparing between the linear and nonlinear Langmuir’s isotherm, q_{max} values obtained are respectively 12.99 and 2.05 mg/g. It can be recalled that, during the kinetics study, the experimental 2nd order q_e value was 3.42 mg/g (Table 1) and close to nonlinear predicted q_{max} 2.05 mg/g. Linear Langmuir predicted q_{max} of 12.99 is thus overestimated and this finding indicates that the fixing of linear isotherm models cannot conclude the complete investigation of adsorption. To visualize the comparisons, the experimental and predicted q_e Vs C_e using the isotherm models are illustrated in Fig. 5. Fig. clearly shows the better fit isotherm is in the sequence of non-Linear Langmuir, Linear Freundlich, Linear Freundlich and non-Linear Langmuir. The adsorption favourability was also checked by another parameter R_L[12] using the equation

$$R_L = \frac{1}{bC_0} \tag{11}$$

where C_o is the initial concentration of the adsorbate (F^-) of the experimental range. For the initial F□ concentration range (1-20 mg/L), the R_L value ranges from 0.0861 to 0.653 suggesting favourable adsorption. The Freundlich constant 1/n value of 0.82 and 0.63 for linear and non-linear Freundlich isotherm, which are less than 1 also confirms the favourability of F^- adsorption on PANI-Cl-jute. Other similar findings for adsorption obeying both Langmuir and Freundlich isotherm includes La(III)- Al(III) loaded scoria adsorbent[12], conducting polymer/bio-polymer composites[9,10], etc. Such fixing of adsorption data on both Langmuir and Freundlich’s isotherm suggests that the surface of PANI-Cl-jute is not completely but partially homogenous and heterogeneous.

Table 2 Comparison between Langmuir and Freundlich’s isotherm coefficient

Sn	Isotherm	Slope	Intercept	R^2	q_{max} (Langmuir)/ K_f (Freundlich)	b (Langmuir)/ 1/n (Freundlich)	λ^2
1	Linear Langmuir	3.306	0.077	0.991	12.99	0.02	0.099
2	Linear Freundlich	0.808	-1.238	0.970	0.29	0.82	0.174
3	Non-Linear Langmuir	-	-	0.988	2.05	0.20	0.041
4	Non-Linear Freundlich	-	-	0.962	0.36	0.63	0.186

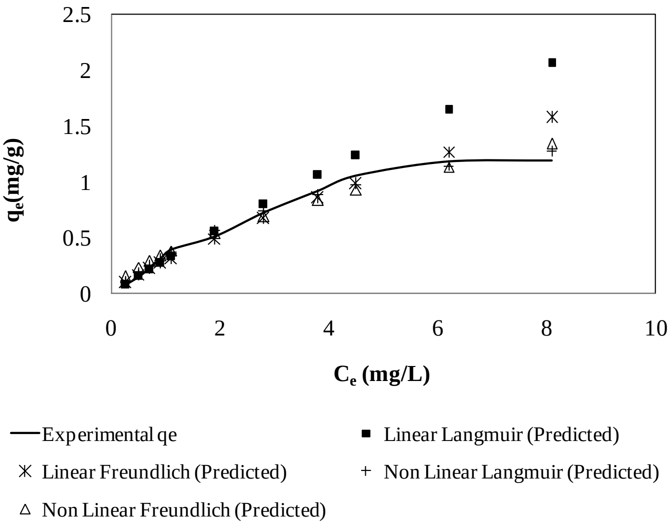

Fig. 5 Comparision between actual and predicated q_e value of Langmuir and Freundlich’s isotherm

3.4 Desorption study

Desorption study was conducted with base (NaOH) of varied strength (0.1, 0.2, 0.5, 1 and 2 M) to deprotonate the adsorbent and recover the adsorbed F□. The desorption experiments were also conducted in a varied volume of 50 - 200 mL maintaining the volume ratio (VR) of adsorption/desorption between 2.5- 10. As can be seen in Table 3, with the increase in strength of NaOH from 0.1 to 2 N, the performance of desorption increased from 12.5 to a range of 88.75 – 97.5% at VR: 2.5- 10. This finding provides evidence in confirming the chemical adsorption mechanism of F□ on PANI-jute-Cl. Using 2 M NaOH, F^- was able to desorb and concentrate only on 2.5% and 10% of adsorption volume along with effective desorption of 97.5% and 88.75% respectively. This effective desorption ability led to the reuse of PANI-Cl-jute for more than 7 recycles effectively and increase the F□ adsorption capacity from 3.42 to 22.80 mg F^-/g. Such high adsorption capacity is much higher than another polymer-based adsorbent like another doped polyaniline with 0.78 mg/g[9], 6.6 mg/g and 8 mg/g respectively by conducting polymer and alumina composites[11] and are much higher than many activated carbons which are below 2 mg/g[18]. By the tenth (10) cycle, the PANI-Cl-jute starts leaching the polymer on solution due to repeated exposure to acid and base.

Table 3 Desorption (%) by different strength and volume of NaOH

Strength of NaOH (N)	Volume ratio of adsorbent /desorbent (VR)		
	2.5	5	10
0.1	12.50	12.50	12.50
0.2	50.00	48.75	46.25
0.5	65.00	63.75	60.00
1	90.00	88.75	85.00
2	97.50	95.00	88.75

4. CONCLUSION

An extensive study was carried out to enhance the adsorption of F^{-} through doping of chloride on polyaniline polymer synthesized on the surface of the jute fiber. The F^{-} adsorption follows Lagergren's pseudo-second-order equation with R^2 of 0.993 – 0.999 suggesting the predominant chemical adsorption behavior on PANI-Cl-jute. The adsorption can also be explained both by the Freundlich and Langmuir isotherm with maximum monolayer coverage of 3.42 mg/g. 2 M NaOH recovers 97.5% of adsorbed F^{-} and was able to concentrate in 2.5% of the adsorption volume enabling 7 recycles & reuse and increased the total uptake up to 22.80 mg/g. PANI-Cl-jute thus showed a promising alternative adsorbent for the effective treatment of F^{-} contaminated water.

REFERENCES

1. Goswami A, Purkait MK (2014) Removal of fluoride from drinking water using nanomagnetite aggregated schwertmannite. J Water ProcEngg 1:91–100.
2. Chen N, Zhang Z, FengCh, Suguira N, Li M, Chen R (2010) Fluoride removal from water by granular ceramic absorption. J. Colloidal Interface Sci 348: 579-584.
3. Rathore V., Dohare D., Mondal P (2016) Competitive adsorption between arsenic and fluoride from binary mixture on chemically treated laterite. J. Environ Chem. Engg. 4: 2417-2430.
4. Zendehdel M, Yeganesh S.B., Khanmohamadi H., Cruciani G. (2017) Removal of Fluoride from aqueous solution by absorption on NaP:HApnanocomposite using response surface methodology. Proc Safety and Environ Protec 109:172-191.
5. Meenakshi S and Viswanathan N (2007) Identification of selective ion-exchange resin for fluoride sorption. J Colloid InterfSci 308:438-450.
6. Amor Z, Bariou B, Mameri N, Taky M, Nicolas S, Elemidaui A (2001) Fluorire removal from Brackish water by electro dialysis. Desalination 133:215-223.
7. Shen J and Schafer A (2014) Removal of Fluoride and Uranium by Nano filtration and reverse osmosis review. Chemoshpere 117:679-691.
8. Zhu, T., Zhu T., Gao J., Zhang L., Zhang W. 2017. Enhanced adsorption of fluoride by cerium immobilized cross-linked chitosan composite, Journal of Fluorine Chemistry, Volume 194, P. 80-88.
9. Karthikeyan M., Satheeshkumar K.K., Elango K.P. (2009) Defluoridization of water via doping of polyanilines. J. Hazard. Mat 163:1026-1032.
10. Karthikeyan M., Satheeshkumar K.K., Elango K.P. (2011) Batch sorption studies on the removal of fluoride ions from water using eco-friendly conducting polymer/bio-polymer composite. Desalination 267:49-56.
11. Maliyekkal, S.M., Sharma, A.K. and Philip, L. (2006). Manganese-oxide-coated alumina: a promising sorbent for defluoridation of water, Water Res., 40. 3497-3506.
12. Subramanium E and Ramalakshmi D.R. (2010) Pristine, purified and polyaniline coated tamarind seed biomaterial powders for defluoridization: Synergism and enhancement in fluoride adsorption by polyaniline coating. J. Sci and Indus. Res. 69: 621-628.
13. Pipileima S, Kumar PA (2017) Kinetics study of fluoride uptake by functionalized polymer polyaniline synthesized on Jute Fibre. J Basic and App Eng Res 3:1136-1139.
14. Nur T, Loganathan P, Nguajen TC, Vigneswaran S, Singh G, Kandaswamy J (2014) Batch and column absorption and desortion of Fluoride using hydrous ferric oxide solutions chemistry and modelling. ChemEngg J. 247: 93-102.
15. Mayorga C. K, Petriciolet B.A, Ruiz F.J.S, Perez M.J, Anila H.E.R, Villarreal IA, Castillo M.D.I (2015) Breakthrough curve modelling of liquid phase absorption of Fluoride ions on aluminium doped bone char using micro-columns: Effectiveness of data fitting approaches. J. Molecu. Liq 208:114-121.
16. Mateus D.M., Pinho H.J (2010) Phosphorous removal by expanded clay-Six year of Pilot scale constructed wetlands experience. Water Environ. Res. 82:128-137.
17. Mucha M., Wankowicz K., Balcerzak J. (2007) Analysis of water adsorption on chitosan and its blends with hydroxypropyl cellulose. e-Polymers 16:1-10.
18. Rao K., Mallikarjum M. (2014) Effective low cost adsorbents for removal of fluoride from Water: A review. Inter. J. Sci. 3:2319-7064.
19. Rathore V., Dohare D., Mondal P (2016) Competitive adsorption between arsenic and fluoride from binary mixture on chemically treated laterite. J. Environ Chem. Engg. 4: 2417-2430.
20. Rout P. R, Bhunia P, Roshan D.R (2017) Evaluation of kinetic and statistical models for predicting breakthrough curves of phosphate removal using dolochar-packed columns. J WatProcEng 17:168–180.
21. Mayorga C. K, Petriciolet B.A, Ruiz F.J.S, Perez M.J, Anila H.E.R, Villarreal IA, Castillo M.D.I (2015) Breakthrough curve modelling of liquid phase absorption of Fluoride ions on aluminium doped bone char using micro-columns: Effectiveness of data fitting approaches. J. Molecu. Liq 208:114-121.

22. Roy S, Das P, Sengupta S, Manna S (2017) Calcium impregnated activated charcoal: Optimization and efficiency for the treatment of fluoride containing solution in batch and fixed bed reactor. Proces Safe and Env Protect 109:18–29.
23. Sehn P (2008) Fluoride removal with extra low energy reverse osmosis membrane: three years of large scale field experience in Finland. Desalination 223:73-84.