Journal of Basic and Applied Engineering Research
p-ISSN: 2350-0077; e-ISSN: 2350-0255; Volume 3, Issue 12; October-December, 2016, pp. 1136-1139

http://www.krishisanskriti.org/Publication.html

Kinetics Study of Fluoride Uptake by Functionalized Polymer Polyaniline Synthesized on Jute Fibre

Sarungbam Pipileima[1] and Potsangbam Albino Kumar[2]

[1,2]National Institute of Technology Manipur
E-mail: [1]spipileima@gmail.com, [2]albinoiit@gmail.com

Abstract—*An amine based functionalized polymer polyaniline synthesized on surface of jute fibre (PANI-jute) was studied for fluoride uptake. The effect of contact time at different fluoride initial concentration was carried out with 5 ppm, 10 ppm and 20 ppm. The adsorption equilibrium time were observed to be between 60 to 120 min for all initial fluoride 5 – 20 ppm, suggesting rapid adsorption. The removal (%) of fluoride ions decreased from 70% - 50% with increase in F^{-} concentration from 5 - 20 ppm. It's due to lower F^{-} concentration which are bound to have more active sites to adsorb than higher concentration. However, the amount of ions adsorbed per gram of adsorbent (q_e) showed increased q_e from 2 - 14 mg/g with the increase in initial F^{-} concentration. The adsorption kinetic studies were carried out with - Elovich and Diffusion model. The correlation coefficients (R^2) for Elovich model were above 0.95 for all the different concentration whereas for diffusion model, R^2 were less than 0.65 signifying the adsorption data better fixing on Elovich model. Also, to identify the best fitting of data numerically, chi-square (χ^2) error analysis was conducted and lower χ^2 value of 0.004 - 0.013 were observed for Elovich model as against 0.095 - 1.944 for Diffusion model. The result obtained showed that adsorption kinetics of fluoride by PANI-jute followed the Elovich model suggesting predominant mechanism of chemical adsorption of F^- rather than physical adsorption.*

Keywords*: Adsorption, Polyaniline, Elovich, Diffusion, Chi-square.*

1. INTRODUCTION

Fluoride in the drinking water may be beneficial and detrimental depending on its concentration. The World Health Organization set a permissible limit at 1.5 mg/l for drinking water [1]. Long term ingestion of high fluoride drinking water causes dental fluorosis or skeletal fluorosis. Fluoride enters the body through water, food, industrial exposure, etc. [2]. Therefore, it is necessary to remove excess fluoride from drinking water. There are several practices for defluoridization such as chemical precipitation [3], ion-exchange [4], reverse osmosis [5], nano-filtration [6] and adsorption [7]. Out of these, adsorption is most extensively used practice. The efficiency of adsorption depends on contact time, temperature, pH, adsorbent and many others. Widely used adsorbents are activated alumina [7], bone char [8], resin [9], activated carbon [8], and plant materials such as nut cell, egg shell, rice husk, tea waste. etc., have been used for fluoride removal. Recently conducting defluoridization using polymer adsorbents are reported viz., polyaniline (PANI) [10-11], polypyrrole (PPy) [12]. These polymers synthesized over the surface of alumina [10-12], chitosan [13], and tamarind seed [14]. The amount fluoride adsorbed on PANI- alumina, PANI- chitosan and PANI- purified tarmarind seed were found to be 6.6 mg/g, 5.9 mg/g and 7.84 mg/g respectively.

This study also deals with Polyaniline (PANI) polymer synthesised on the surface of jute fibre for defluoridation and the important objective is the equilibrium and kinetics aspects of the adsorption of fluoride. Various fluoride ion concentrations at different contact time were investigate to identify adsorption equilibrium time and its appropriate kinetic models.

2. MATERIALS AND METHODS

2.1 Materials and Estimation

Chemicals like NaF, HCl, Aniline, Ammonium Peroxydisulphate and all other chemicals were used of analytical grade. Aniline was distilled prior to use and before distillation KOH is added in order to remove the excess water molecule if present. Synthetic solutions were made in the laboratory for the experiment. Used Jute fibre was washed and used for coating and synthesizing the polymer. For preparing synthetic solution of fluoride, Sodium fluoride having molar mass of 42 g/mol is used. TISAB II was added and estimated the fluoride using fluoride meter. The stock solution and other fluoride standards are kept in plastic ware.

2.2. Preparation PANI-jute fibre

Polyaniline was synthesized by oxidation of aniline in presences of 1, 4 – phenylenediamine, a chain terminator in acidic medium in presence of oxidant, ammonium peroxydisulphate. 20ml of Aniline and 3.3gm of 1, 4 – phenylenediamine were dissolved in 660ml of 1M HCl. The mixture was cooled using iced bath followed by addition of 50gm jute fibres and stirrer for 5 min. The reaction started after addition of pre-cooled solution of 16.2gm of ammonium peroxydisulphate and 160ml of 1M HCl. The reaction mixture was maintained at cooled temperature around 5°C and kept for overnight. Then the jute fibre was washed with distilled water and soaked it in the 2M ammonia solution for one night. Then wash the jute fibre with distilled water to adjust the solution to neutral pH. Finally, the blue black coloured PANI-jute fibre was dried in the sunlight. [15]

3. RESULTS AND DISCUSSION

3.1 Effect of contact time and initial concentration

The study for effects of contact time on adsorption and also for different initial concentration of F^- ions was carried out by contacting with 4 g/L of PANI-jute with 5, 10 and 20 ppm of fluoride ions. The findings are presented in Fig. 1. It has been observed that the adsorption took place rapidly within the first 40 minutes for all different initial concentration with 10 to 50% for initial F^- 5 - 20 ppm and adsorption equilibrium time was almost 60 - 120 min for all initial fluoride concentration. The removal (%) of fluoride decreased from 70 -50% with increased in initial F^- concentration from 5 -20 ppm. Lower F^- concentrations were obvious to have more sites to adsorb and thus 5 ppm F^- concentration has higher removal (%) than 20 ppm F^- concentration.

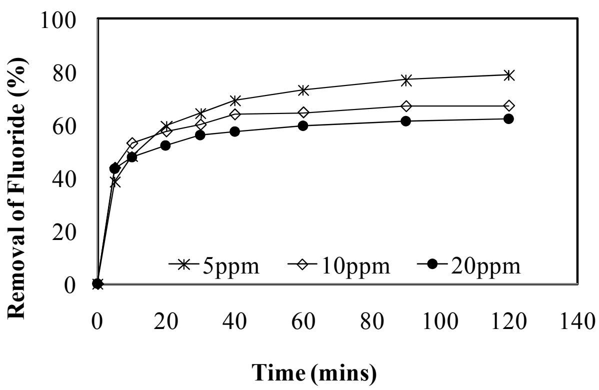

Fig. 1: Effect of contact time on the PANI jute fibre

However, the amount of ions adsorbed per gram of adsorbent at time t (q_t) showed opposite trend unlike removal (%) with the value increases from 2 mg/g to 14 mg/g with the increase in initial F^- concentration from 5 ppm to 20ppm (Fig. 2). Higher F^-concentration are bound to get more adsorbed due to overcrowding effect and amount of ions adsorbed per gram of adsorbent increased with higher increase in F^- initial concentration.

[16]

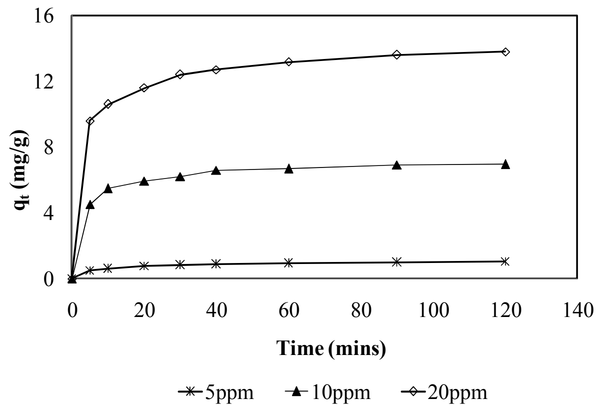

Fig. 2: Effect of contact time on the amount of F^- ions adsorbed onto PANI Jute fibre

3.2 Adsorption kinetics

Kinetics of adsorption gives the rate of uptake amount of ions or adsorbed from the solution. In order to identify the kinetics of adsorption, the data were analysed using two kinetics model namely Elovich [17] and Diffusion kinetics [18] model.

Elovich kinetics model can be represented in the form of equation

$$q_t = \beta \ln(\alpha\beta) + \beta \ln(t) \quad (1)$$

where q_t (mg/g) is the amount of adsorbed at time, t, 'α' (mg/g min) is the initial sorption rate and 'β' (g/mg) is the desorption constant.

The graph for Elovich model was plotted in Fig. 3 and observed that the correlation coefficient (R^2) value for all the different concentration is above 0.95. This suggests that the adsorption kinetics obeys the Elovich model. The evaluated value of 'α' and 'β' for Elovich model are shown in Table 1 for comparison with that of Diffusion model coefficients.

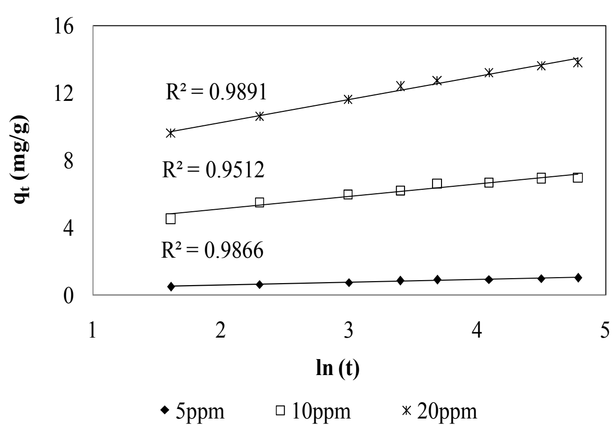

Fig. 3: Elovich kinetics model for the adsorption of fluoride on PANI jute fibre

The diffusion kinetics model is also represent in linear form and is given by the equation,

$$q_t = K_d\, t^{1/2} + C \quad (2)$$

where q_t (mg/g) is the amount of adsorbed ions at time t, 'K_d' (mg/g min$^{1/2}$) is the diffusion rate constant and 'C'(mg/g) is the diffusion constant [18]. The value of K_d and C were given by slope and the intercept of the linear plot of q_t vs. $t^{1/2}$ respectively. Diffusion kinetics model for experimental value is shown in Fig. 4. It was observed that R^2 value for all initial concentrations were less than 0.95. The evaluated coefficients of diffusion model 'C' and 'K_d' are shown in Table 2.

Table 1: Elovich kinetics of PANI jute fibre

C_o	Elovich				
	slope	intercept	α	B	χ^2
5	0.1693	0.2473	25.452	0.169	0.004
10	0.747	3.6033	166.564	0.747	0.042
20	1.3593	7.5329	187.688	1.359	0.013

Table 2: Diffusion kinetics of PANI jute fibre

C_0	Diffusion				
	slope	Intercept	k_d	C	χ^2
5	0.0838	0.2703	0.0838	0.2703	0.095
10	0.5073	2.6653	0.5073	2.6653	1.171
20	0.9855	5.3713	0.9855	5.3713	1.944

For better comparison between Elovich and Diffusion model, the predicted q_t value for each are plotted against the experimental q_t value for all the initial F^- concentrations and are shown in Fig. 5. The predicted q_t value of Elovich model are observed to be much closer to that of Diffusion model suggesting a better fit adsorption kinetics on Elovich model.

Several researchers had also employed several analytical equation/models to analyse the fixing of data in adopted model such as Chi square- error analysis [19]. The mathematical equation for chi-square is

$$\chi^2 = \sum \frac{(q_{e(exp)} - q_{e(pre)})^2}{(q_{e(exp)})} \quad (3)$$

where $q_{t(pre)}$ is the predicted amount of ions adsorbed per gram of adsorbent at time 't' using the models and $q_{t(exp)}$ is experimental amount of ions adsorbed per gram of adsorbent at time 't'. The evaluated χ^2 values for both Elovich and Diffusion were shown in Table 1 and 2 respectively. The χ^2 value for Elovich is 0.004 to 0.042 as against 0.095 to 1.944 for Diffusion model indicating very insignificant error for Elovich model. This investigation further concludes the adsorption kinetics of fluoride adsorption on PANI-jute can be explained by Elovich model. Further, this finding suggests the predominant chemical adsorption behavior of fluoride on PANI-jute and insignificant physical adsorption or diffusion.

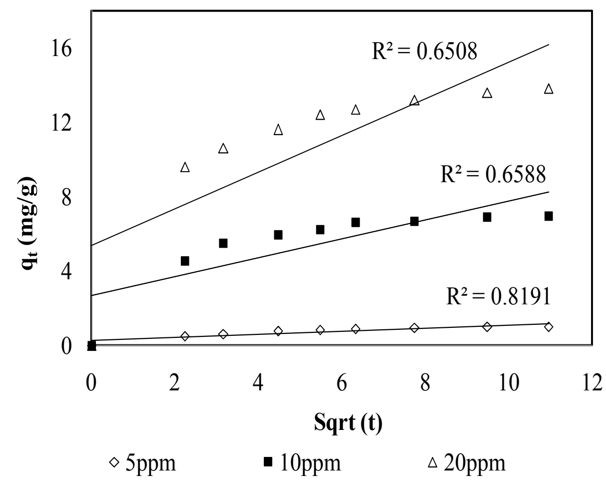

Fig. 4: Diffusion kinetics model for the adsorption of fluoride on PANI jute fibre

In addition to this, the rapid adsorption within the first 40 minutes for all different initial concentration of fluoride ions indicates the readily active sites of amines of the polymer to bind with fluoride ions. Very less or almost insignificant adsorption after 60 minutes along with inability of the adsorption kinetic data to fit in diffusion model explains the non physical adsorption. Jute fiber, which is the supporting material for the polyaniline are observed to adsorbed around 0.05 mg/g of fluoride when employed as an adsorption due to its surface area and diffusion. Therefore, such insignificant physical adsorption on PANI-jute suggests the effective coating of polyaniline on surface of jute fiber. However further analysis will be able to explain the exact characterization of surface area.

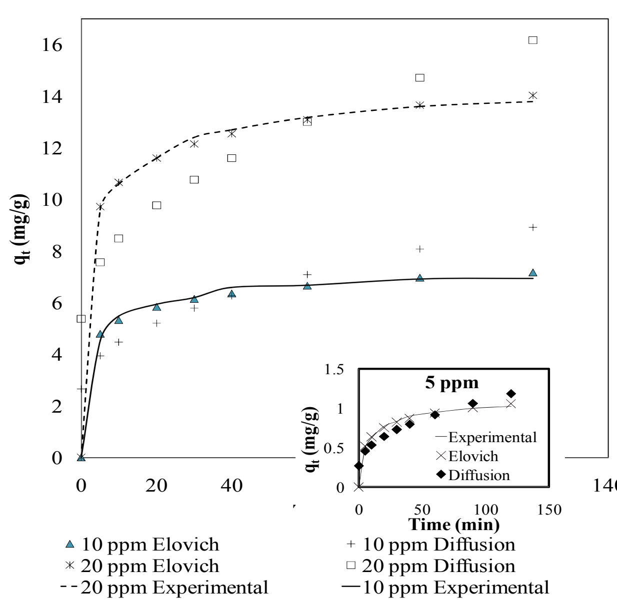

Fig. 5: Comparision between Predicted and Experimental q_t value for Elovich and Diffusion model

4. CONCLUSION

The study reveals the effective coating of polyaniline on surface of jute fiber. Adsorption data show that the adsorption of fluoride ion by PANI–jute from acqueous solution can be describe by Elovich model with predicted amount of ions adsorbed much closer to experimental value and also with insignificant error of 0.004 to 0.42. The kinetic study also showed the rapid adsorption behavior of fluoride ions to PANI-jute due to chemical adsorption with almost insignificant amount of physical adsorption or diffusion.

5. ACKNOWLEDGEMENTS

The author Potsangbam Albino Kumar would like to thank DST/WTI for the funding of the project DST/WTI/2K12/08.

REFERENCES

[1] WHO Report, "Fluoride and Fluorides: Environmental Health Criteria", *World Health Organisation, Geneva,* 1984.

[2] K. Sarala, P. R. Rao, "Endemic Fluorosis in the village Ralla, Anantapuram in Andhra Radesh-an epidemiology study", *Fluoride*, 26, 1993,pp. 177-180.

[3] S. Maurice, O.Y. Kojima, O. Aoyi, C. Eileen, B.H. Matsuda, "Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite", *F-9, J. Colloid Interface Sci*., 2004, pp. 341–350.

[4] Renuka Piddennavar, Pushpanjali Krishnappa, "Review on defluoridation techniques of water", *International Journal of engineering and Science*, vol.2, No.3, 2013, pp. 86-94.

[5] S.V. Joshi, S.H. Mehta, A.P. Rao, A.V. Rao, "Estimation of sodium fluoride using HPLC in reverse osmosis experiments", *Water Treatment*, 7, 1992, pp. 207-211.

[6] R. Simons, "Trace element removal from ash dam waters by nanofiltration and diffusion dialysis", *Desalination*, 89, 1993, pp. 325-341

[7] A.A.M. Daifullah, S.M. Yakout, S.A. Elreefy, "Adsorption of fluoride in aqueous solutions using KMnO4-modified activated carbon derived from steam pyrolysis of rice straw", J. Hazard. Mater, 147, 2007, pp. 633–643.

[8] Herschel S.Horowitz, Stanley B.Heifetz, and William S. Driscoll, "Partial defluoridation of a community water supply and dental fluorosis", *Health service reports*, 87(5), 1972, pp. 451-455.

[9] S. Meenakshi, N. Viswanathan, "Identification of selective ion-exchange resin for fluoride sorption", *Journal Colloid Interface Science,* 308, 2007, pp. 438–450.

[10] M. Karthikeyan, K.K. Satheeshkumar, K.P. Elango, "Defluoridation of water via doping of polyanilines", *Journal Hazardous Material,* 163, 2009, pp. 1026–1032.

[11] M. Mucha, K. Wankowicz, J. Balcerzak, "Analysis of water adsorption on chitosan and its blends with hydroxypropylcellulose", *e-Polymers,* 16, 2007, pp. 1–10.

[12] G. Crini, "Non-conventional low-cost adsorbents for dye removal: a review", *Bioresour. Tech*., 9 (9), 2007, pp. 1061–1085.

[13] M. Karthikeyan, K.K. Satheesh Kumar, K.P. Elango, "Batch sorption studies on theremoval of fluoride ions from water using eco-friendly conducting polymer/bio-polymer composites", *Desalination* , 267, 2011, pp. 49–56.

[14] E Subramanium and R Dhana Ramalakshmi, "Pristine, purified and polyaniline-coated tarmarind seed biomaterial powders dor defluoridation: Synergism and enhanchment in fluoride adsorption by polyaniline coating", *Journal of Scientific & Industrial research*, 69, 2010, pp. 621-628.

[15] P. Albino Kumar, S. Chakraboty, M. Ray, "Removal and Recovery of chromium from wastewater using short chain polyaniline synthesized on jute fibre", *Chemical engineering Journal*, 141, 2008, pp. 130-140.

[16] M. Karthikeyan, K P Elango, "Removal of fluoride from aqueous using graphite: A kinetics and thermodynamic study", *Indian Journal of Chemical Technology*, 15, 2008, pp. 525-532.

[17] D.L. Sparks, "Kinetics of reaction in pure and mixed systems, in Soil Physical Chemistry", Edited by Sparks, D. L., CRC Press, Boca Raton, Florida, 1986,

[18] T.E. Hristova, "Comparison of different kinetic models for adsorption of heavy metals onto activated carbon from apricot stones", *Bulgarian Chemical Communications*, 43 – 3, 2011, pp. 370 – 377.

[19] N. Viswanathan, C.S. Sundaram, S. Meenakshi, "Development of multifunctional chitosan beads for fluoride removal", *Journal of Hazardous Materials*, 167, 2009, pp. 325-331.