FLUORIDE REMOVAL FROM WATER USING NANOSCALE ZERO-VALENT IRON (NZVI)

Hossam S. Jahin

Researcher, Chemistry Department, Central Laboratory for Environmental Quality Monitoring (CLEQM), National Water Research Center, Egypt.
E-mail: hossam_gahin@hotmail.com

ABSTRACT

Excessive intake of fluoride can cause adverse effects on human health. In this study, nanoscale zero valent iron (nZVI) was prepared and applied to remove excessive fluoride from water. The experiments were conducted in a batch system and the effects of pH, contact time, and the concentrations of fluoride and nanoscale zero valent iron doses were investigated. Transmission Electron Microscope (TEM) images show synthesized nanoscale zero-valent iron (nZVI) has a size in the range of 50–100 nm. The experimental results revealed that the removal efficiency of fluoride was increased with increasing nanoscale zero valent iron (nZVI) dosage and reaction time, but decreased with increasing initial concentration and initial solution pH. The removal rate of fluoride reached 84 % in 35 min with nanoscale zero valent (nZVI) dosage of 0.6 g/l and pH 4. The isothermic data were found to be well described by Freundlich model. The maximum loading capacity as estimated by Langmuir model was 18.91 mg/g. Overall, the results obtained indicate that nanoscale zero valent iron (nZVI) could be effectively used for removal of fluoride from contaminated water.

Keywords: Fluoride, Removal, Water, Nanotechnology, Iron nanoparticles.

Received 6May,2014. Accepted18 July,2014

1. INTRODUCTION

Fluoride contamination of drinking water has raised health concerns, due to excess intake of fluoride can cause adverse effects to human beings such as dental and skeletal fluorosis, infertility, brain damage, and thyroid disorder (Bhatnagar et al. [1]; Meenakshi and Maheshwari [2]). The acceptable fluoride concentration in drinking water is generally in the range of 0.5 to 1.5 mg/l (WHO [3]).

Studies have shown that major of the kidney diseases have a great inclination of toxicity of fluoride. High doses and short term exposure to fluoride can reduce or severely impair kidney function. Several research groups have also shown that fluoride can interfere with the function of pineal gland as well as the brain. The pineal gland is one of the major sites where fluoride is accumulatedin body having concentrations higher than that of teeth and bones. Other research has indicated that workers who are exposed to high fluoride concentration are more prone to be diagnosed with bladder cancer (Islam and Patel [4]). There are more than 20 developed and developing nations that are endemic for fluorosis. These are Argentina, U.S.A., Morocco, Algeria, Libya, Egypt, Jordan, Turkey, Iran, Iraq, Kenya, Tanzania, S. Africa, China, Australia, New Zealand, Japan, Thailand, Canada, Saudi Arabia, Persian Gulf, Sri Lanka, Syria, India, etc. (Mameri et al. [5]). Therefore, it is extremely important to develop cost-effective technologies for the removal of fluoride from contaminanted water in order to minimize the risk to humans.

Nanotechnology is an enabling technology that could potentially lead to cost-effective and high performance water treatment systems. Nanoscale particles have a large surface area, available for interaction with contaminants, high surface reactivity and could provide cost effective solution to many challenging environmental remediation problems (Zhang [6]). For example, nanoparticle zero valent iron (nZVI) of a diameter 1-100 nm and with a surface area in the range 20-40 m^2/g, provide 10-1,000 times greater reactivity than granular iron, which has a surface area < 1 m^2/g (Wang and Zhang [7]). Nanoparticle zero valent iron (nZVI) have been shown to be effective in the treatment of a wide variety of common environmental contaminants such as chlorinated organic solvents, organochlorine pesticides, and polychlorinated biphenyls (Mayo et al. [8]; Liu et al. [9]; USEPA [10]), heavy metals and radionuclides, (Li and Zhang [11]; Kanel et al. [12]; Uzum et al. [13]; Sun et al. [14]; Li and Zhang [15]; Elebi [16]) in both *ex-situ* and *in-situ* (e.g. via direct injection to subsurface environments) applications (Cundy et al. [17]). In this paper, the parameters which affect on the effectiveness of fluoride removal from water by synthesized nanoscale zero valent iron (nZVI) were studied. These parameters include pH, dosage of nanoscale zero valent iron (nZVI) and fluoride concentrations. The purpose of this study is to improve our understanding the removal of fluoride by nanoscale zero valent iron (nZVI).

2. MATERIALS AND METHODS

2.1. Chemicals and materials

All chemicals used were analytical grade. Chemicals used in the synthesis of zero valent iron nanoparticle (nZVI) as adsorbent were ferric chloride ($FeCl_3.6H2O$), sodium borohydrate ($NaBH_4$), and ethanol.

2.2. Method for nanoscale zero valent iron (nZVI) synthesis

Synthesis of nanoscale zero valent iron (nZVI) is based on borohydride reduction of Fe (III) (Yuvakkumara [18]) according to the following reaction (Galvee et al.[19]):
$4Fe^{3+}$ (aq) + $3BH_4$ + 9H2O → $4Fe^0$ (s) + $3H_2BO_3$ + $12H^+$ (aq) + $6H_2$ (g) (1)

2-2-1-Procedure:

0.5406 g $FeCl_3.6H2O$ was dissolved in a solution containing 24 ml ethanol and 6 ml distilled water and stirred well. 0.3783 g sodium borohydride was dissolved in 100 ml distilled water and added to the first solution drop wise (1drop/ 2 seconds). Slowly the solution turned to black colour. This solution was stirred for 10 minutes before it was filtered under vacuum. The residue was washed three times sequentially with 25 ml ethanol. The particles were dried at 50˚C in an oven overnight. The surface morphology of nanoscale zero valent iron was observed with transmission electron microscope (TEM, JEM-2100 HR, 200 kV)

2.3. Preparation of aqueous fluoride solution

A 100 mg/ L fluoride stock solution was prepared by dissolving 0.221g of NaF in 1L of double distilled water. The experimental solutions were prepared by appropriate dilutions of the above solution. Various concentrations (2.5-20 mg/L) of fluoride solutions were prepared by this stock solution.

2.4. Batch adsorption experiments

All the experiments were carried out in 250 mL conical flasks with 100 mL test solution at room temperature (25±2 °C). The flasks, along with test solution and 0.5 g of the adsorbent at different pH from 3 to 10, were shaken in horizontal shaker at 150 rpm to study the equilibration time (5-50 min) for maximum adsorption of fluoride and to calculate the kinetics of adsorption process. At the end of the desired contact time, the samples were filtered using Whatman no. 42 filter paper and the filtrate was analyzed for residual fluoride concentration by Ion Chromatography (IC), Dionex product, model DX5000.

The adsorption capacity q_e (mg/g) of the adsorbent was calculated from the following equation

$$q_e = (Ci - Ce)V/W; \tag{2}$$

$$\text{Removal efficiency \%} = (Ci - Ce)\,100/\,Ci \tag{3}$$

Where *Ce* is the residual concentration reached at equilibrium state, *Ci* is initial fluoride concentration and *V* is the volume of solution (l) and *W* is the weight of adsorbent (g).

3. RESULTS AND DISCUSSION

3.1. Characterization of nanoscale zero valent iron (nZVI)

The size of iron nanoparticles were determined using transmission electron microscopy (TEM, JEM-2100 HR), with an acceleration voltage of 200 kV. Fig. 1 shows TEM images of the synthesized nanoscale zero valent iron (nZVI). The particles ranged in size from 50 to 100 nm. The nZVI tends to form a chain-like aggregate due to the electrostatic force between particles. These chain-like nano iron aggregates were also observed by some other researchers (Wang and Zhang [7]; Tai and Shih [20]; Phenrat et al. [21]). This result suggests that the particles are easily aggregated and do not exist in individual forms due to spontaneous aggregation of nanoparticles (Liou et al. [22]). Moreover, surface morphology shows that there exist two layers in the nZVI particle. The core or inside layer represents the Fe^0, and the outer layer iron-oxide(s).

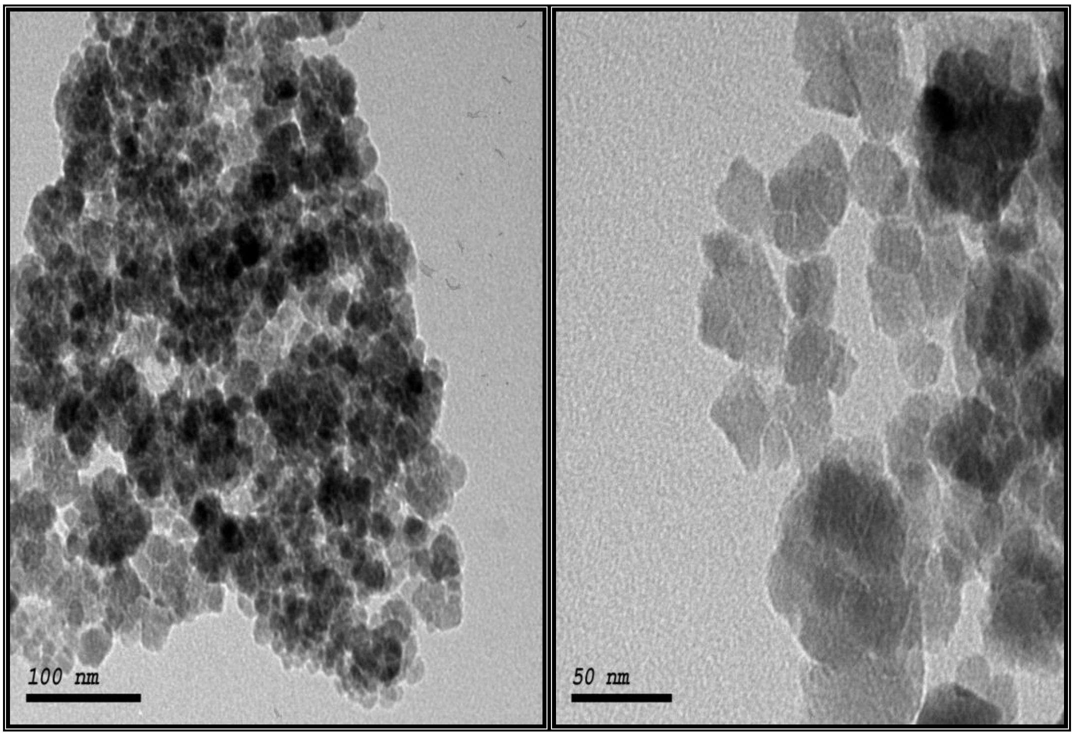

Fig.1: TEM images of synthesized nanoparticle zero valent iron (nZVI)

3.2. Effect of pH

Effect of pH on the removal of fluoride on nanoparticle zero valent iron (nZVI) was investigated. Experimental studies were carried out at room temperature with an initial fluoride concentration of 5 mg/l using an adsorbent of 0.5 g/l, and an agitation speed of 150 rpm for 30 min. The adsorption results are shown in Figure 2. In Figure 2, the results show that the fluoride adsorption efficiency was very high at low pH and decreased with an increase of pH. That is attributed to columbic force between the positively charged surface of adsorbent (nZVI) and negatively charged fluoride ions (Karthikeyan and Ilango [23]). The maximum value of fluoride adsorption efficiency occurred at pH 4.0.

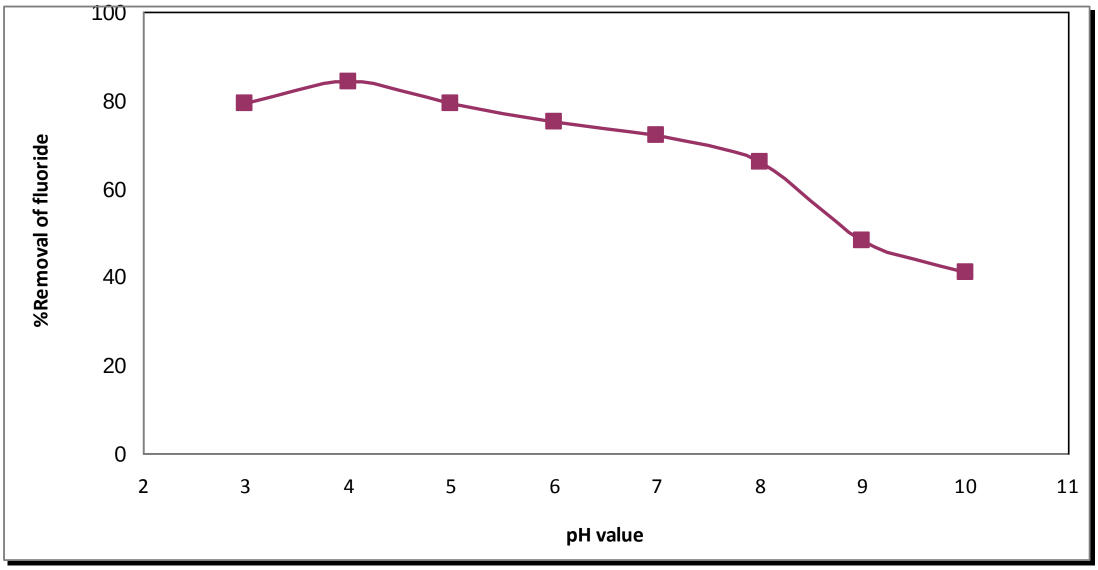

Fig. 2: Effect of pH on % fluoride removal.

3.3. Effects of contact time

Experiments were carried out at room temperature with an initial fluoride concentration of 5 mg/l using an adsorbent dosage of 0.5 g/l at pH 4.0 and an agitation speed of 150 rpm for contact times of 0, 5, 10, 15, 25, 30, 35, 40, 45 and 50 min. Results for the removal efficiency of fluoride are shown in Figure 3. In Figure 3, illustrates that the removal percent of fluoride increased rapidly during the initial 35 minutes. Thereafter, the removal of fluoride was almost constant. During the initial stage of sorption, a large number of vacant surface sites were available for adsorption. After a lapse of some time, the remaining vacant surface sites were more difficult to occupy due to repulsive forces between the adsorbed molecules on the solid surface and in the bulk phase or desorption (Lu et al. [24]).

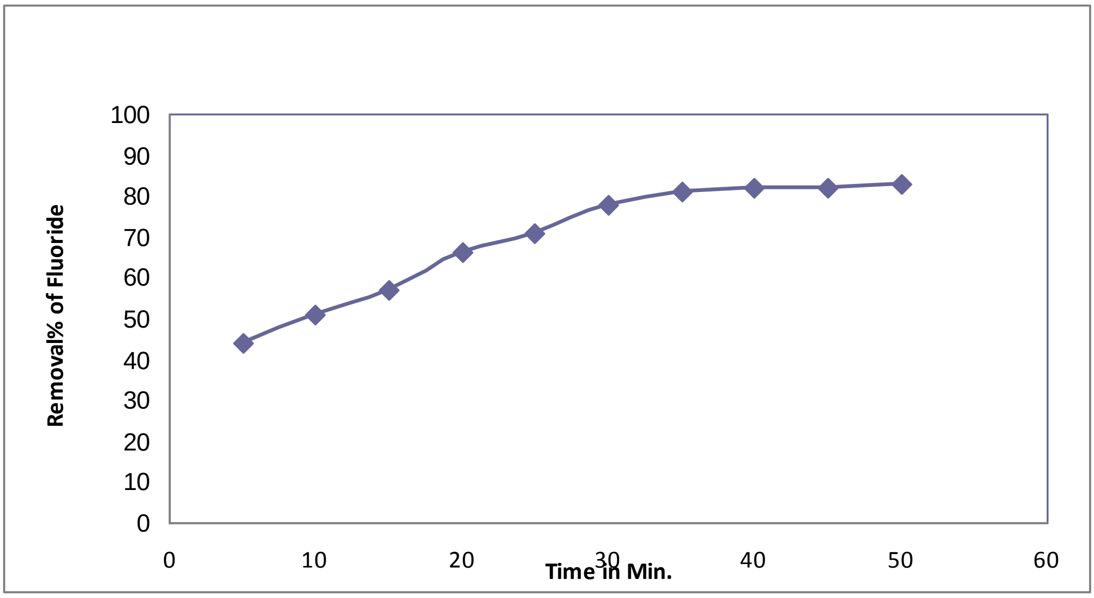

Fig. 3: Effect of contact time

3.4. Effect of adsorbent doses

The effect of adsorbent doses was studied by varying the adsorbent quantity from 0.1 to 1.0 g maintaining the initial fluoride concentration 5 mg/l, at room temperature, pH4 and an agitation speed of 150 rpm. The results are shown in figure 4. The removal efficiency of fluoride increased with increasing adsorbent dose due to the increased availability of adsorption sites. Therefore in order to achieve maximum removal efficiency, 0.6 g dose of adsorbent was sufficient for the fixed initial concentration of fluoride (5 mg/l). The adsorption amount (mg/g) increases with increase in adsorbent dosage, possibly due to the fact that some adsorbent sites are saturated at higher adsorbent dose (Fakhri and Adami [25]).

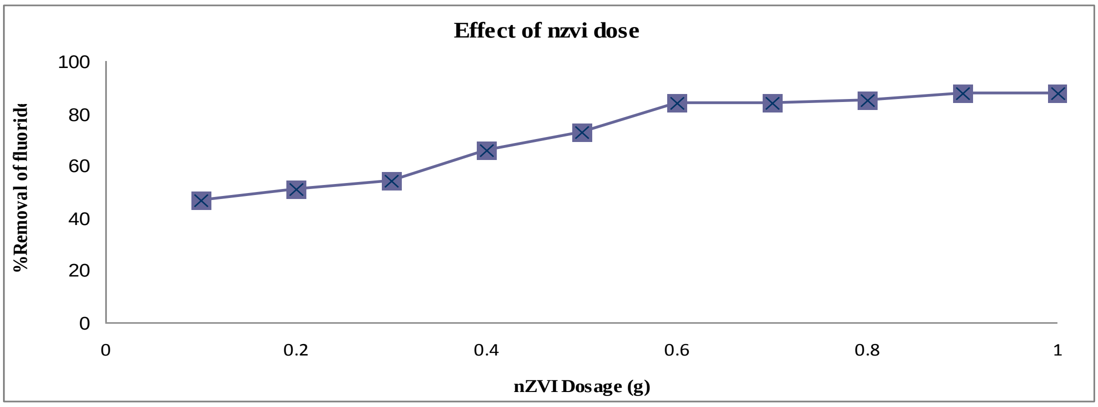

Fig. 4: Effect of nzvi doses

3.5. Effect of initial fluoride concentrations

Studies on the effect of initial fluoride concentration were conducted at 2.5, 5.0, 10 and 20 mg/l of fluoride keeping adsorbent dose of 0.6 g/l, pH of 4, stirring rate of 150 rpm. The results are showed in figure 5. The data presented in figure 5 indicate that the percentage removal of fluoride ion decreases with increase in initial fluoride ion concentration. This is probably due to the fact that for a fixed adsorbent dose, the total available adsorption sites are limited, thereby adsorbing almost the same amount of fluoride.

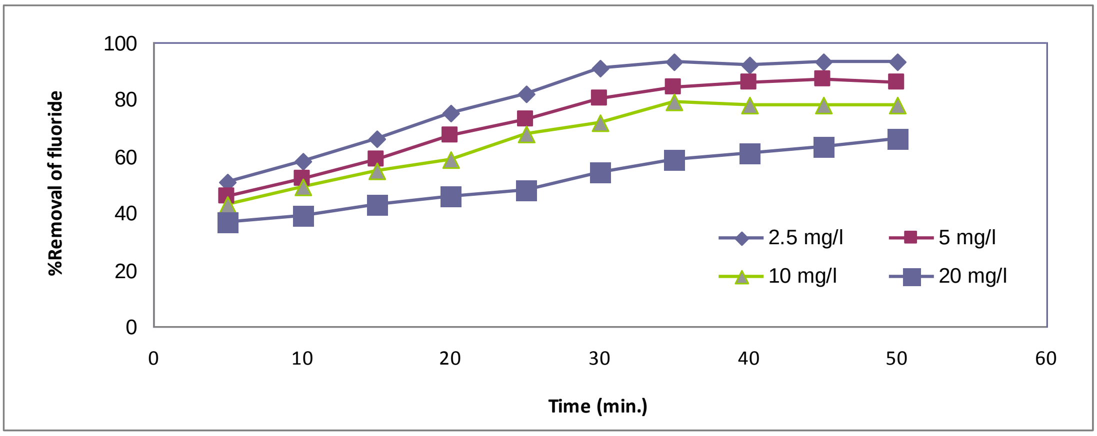

Fig. 5: Effect of initial fluoride concentration

3.6. Adsorption isotherms

The relationship between the amount of substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm (Alkan et al. [26]). Langmuir and Freundlich models of isotherms have been tested in the present study figure 6 and 7. The Langmuir model is applicable to homogenous adsorption, which can be expressed by the following equation (Langmuir [27]):

$$q_e = q_{max}\, bc_e/1+bc_e \qquad (4)$$

On the other hand, the Freundlich model is used to describe the heterogeneous adsorption, which is shown as below (Freundlich [28]):

$$q_e = K_f\, c_e^{1/n} \qquad (5)$$

Where q_m is the maximum adsorption capacity (mg/g), c_e is the equilibrium concentration of adsorbate (mg/l), q_e is the adsorption capacity (mg/g), b is adsorption reaction constant (l/mg), and K_f and n are empirical constants.

Table 1.Model parameters of Langmuir and Freunlich isotherms.

Langmuir model	q_m	B	R^2
	18.91	0.66	0.963
Freundlich model	K_f	N	R^2
	3.32	2.15	0.998

The constants of both models are summarized in Table 1. According to the correlation coefficient (R^2), Freundlich model is much better in description of adsorption isotherm data with a higher R^2 than Langmuir model. Similar conclusions were drawn from studies on fluoride removal by different adsorbents such as activated alumina (Ghorai and Pant [29]), hydroxyapatite (Wang et al. [30]), brushite (Mourabet et al. [31]), zirconium-iron oxide (Dou et al. [32]) and high alumina content bauxite (Lavecchia et al. [33]). The value of n is in between 1 and 10 which indicates beneficial adsorption (Milmile et al. [34]). The maximum adsorption capacity under the conditions tested was 18.91 mg/g.

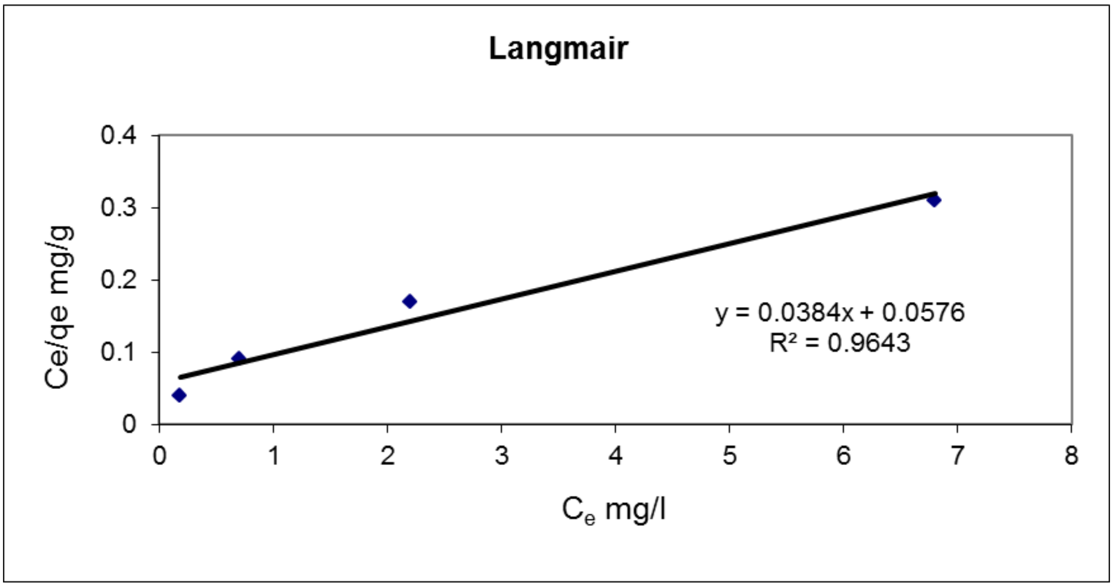

Fig. 6: Langmuir isotherm

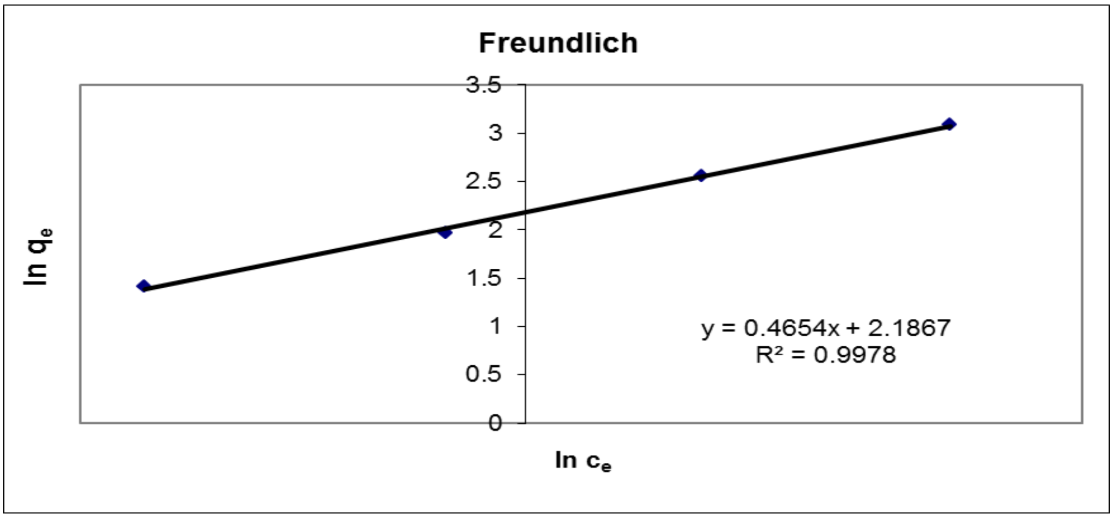

Fig. 7: Freundlich isotherm

CONCLUSION

All adsorption parameters such as pH, contact time, adsorbent dose and initial concentration of fluoride have effect on the removal of fluoride from water by nanoscale zero valent iron (nZVI). The optimal condition for removal of fluoride was pH 4, contact time 35 min. and 0.6 g of nanoscale zero valent iron (nZVI). Freunlich isotherm was well fitted with the experimental data, therefore it was used to explain the adsorption mechanism. The maximum loading capacity as estimated by Langmuir model was 18.91 mg/g. All results conclude that nanoscale zero valent (nZVI) is an effective adsorbent for removal of fluoride from contaminated water.

REFERENCES

[1]. Bhatnagar, A., Kumar, E. and Sillanpaa, M., Fluoride removal from water by adsorption- a review. Chem. Eng. J., 171, 811-840, 2011

[2]. Meenakshi and Maheshwari, R.C. , Fluoride in drinking water and its removal. J. Hazard. Mater. 137, 456-63, 2006.

[3]. WHO, Guidelines for Drinking Water Quality, World Health Organization, Geneva, 2008.

[4]. Islam, M. and Patel, R.K., Thermal activation of basic oxygen furnace slag and valuation of its fluoride removal efficiency. Chem. Eng. J , 169, 68–77, 2011.

[5]. Mameri, N., Yeddou, A.R., Lounici, H., Grib, H., Belhocine, D. and Bariou, B., Defluoridation of septentrional Sahara water of North Africa by electrocoagulation process using bipolar aluminium electrodes, Water Res. 32 (5) 1604–1610, 1998.

[6]. Zhang, W.X., Nanoscale iron particles for environmental remediation: an overview, J. Nanoparticle Res. 5, 323-332, 2003.

[7]. Wang, C.B. and Zhang, W.X., Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs, Environ. Sci. Technol. 31, 2154-2156, 1997.

[8]. Mayo, J.T., Yavuz, C., Yean, S., Cong, L., Shipley, H., Yu, W., Falkner, J., Kan, A., Tomson, M. and Colvin, V.L. , The effect of nanocrystalline magnetite size on arsenic removal, Sci. Technol. Adv. Mater. 8, 71-75, 2007.

[9]. Liu, Y., Majetich, S.A., Tilton R.D., Sholl, D.S. and Lowry, G.V., TCE dechlorination rates, pathways, and efficiency of nanoscale iron particles with different properties. Environ Sci Technol 39: 1338-1345, 2005.

[10]. USEPA, , Nanotechnology white paper. ERA 100/B-07/001. Washington, DC20460: Science Policy Council, U.S. Environmental Protection Agency, 120 pp, 2007.

[11]. Li, X.Q and Zhang, W.X., Sequestration of metal cations with zero valent iron nanoparticles, a study with high resolution X-ray photoelectron spectroscopy (HR-XPS), J. Phys. Chem., 111, 6939-6946., 2007.

[12]. Kanel, S.R.,Manning, B., Charlet, L. and Choi, H., Removal of arsenic (III) from groundwater by nanoscale zero-valent iron. Environ. Sci. Technol., 39, 1291-1298, 2005.

[13]. Uzum, C., Shahwan, T., Eroglu, A.E. and Hallam, T.B., Synthesis and characterization of kaolinite-supported zero-valent iron nanoparticles and their application for the removal of aqueous Cu^{2+} and Co^{2+} ions. Appl. Clay Sci., 43, 172-181, 2009.

[14]. Sun,Y.P., Li, X.Q., Cao, J., Zhang, W.X. and Wang, H.P., Characterization of zero-valent iron nanoparticles, Adv. Colloid. Interface Sci. 120, 47-56, 2006.

[15]. Li, X.Q., and Zhang, W.X., Iron nanoparticles: the core–shell structure and unique properties for Ni (II) sequestration. Langmuir 22, 4638-4642, 2006.

[16]. Elebi, O.C., Uzum, C., Shahwan, T. and Erten, H.N.A., A radiotracer study of the adsorption behavior of aqueous Ba^{2+} ions on nanoparticles of zero-valent iron. J. Hazard Mater., 148, 761-767, 2007.

[17]. Cundy,A. B., Hopkinson, L. and Whitby, R.L. , Use of iron-based technologies in contaminated land and groundwater remediation: a review, Sci. Total Environ. 400, 42-51, 2008.

[18]. Yuvakkumara, R. Preparation and characterization of zero valent iron nanoparticles. Digest Journal of Nanomaterials and Biostructures 6, No 4, 1771-1776, 2011.

[19]. Galvee, G., Kenneth, K., Sorensen, C.M. and Hadjipanayis, G., Chemistry of Brohydride Reduction of Iron(II) and Iron(III) Ions in Aqueous and Nonaqueous Media. Formation of Nanoscale Fe, FeB, and Fe2B powders. Inorg. Chem., 34 (1), 28-35, 1995.

[20]. Tai, Y. and Shih, Y., Debromination of decabrominated diphenyl ether by nanoscale zerovalent iron. 5th International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Monterey, CA, May 22-25, 2006.

[21]. Phenrat, T., Saleh, N., Sirk, K., Tilton, R.D. and Lowry, G.V., Aggregation and sedimentation of aqueous nanoscale zerovalent iron dispersions. Environ. Sci. Technol., 41(1), 284-290, 2007.

[22]. Liou, Y.H., Lo, S.L., Kuan, W.H., Lin, C.J. and Weng, .C., Effect of precursor concentration on the characteristics of nanoscale zerovalent iron and its reactivity of nitrate. Water Res., 40(13), 2485- 2492, 2006.

[23]. Karthikeyan, G. and Siva Ilango, S., Fluoride Sorption using Morringa Indica- ased Activated Carbon. Iran. J. Environ. Health. Sci. Eng., 4, No. 1, 21-28, 2007.

[24]. Lu, D., Q. Cao, Q., Cao, X. and Luo, F. , Removal of Pb(II) using the modified lawny grass: Mechanism, kinetics, equilibrium and thermodynamics studies. J. Hazardous Materials, 166(1), 239-247, 2009.

[25]. Fakhri, A. and Adami, S. , Adsorption behavior and mechanism of ammonium ion from aqueous solution onto nanoparticles zero valent iron. Arbian j. of Chem. In press, 2013.

[26]. Alkan, M., Demibas, S. and Dogan, M. , Removal of reactive blue 221 and acid blue 62 anionic dyes from aqueous solution by sepiolite, Dayes Pigments, 65, 251-259, 2005.

[27]. Langmuir, I. , The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. 57, 1361-1403, 1918.

[28]. Freundlich, H. , Uber die adsorption in 1 osungen (adsorption in solution). Z. Phys. Chem. 57, 384-470, 1906

[29]. Ghorai, S. and Pant, K.K., Equilibrium kinetics and breakthrough studies for adsorption of fluoride on activated alumina. Sep. Purif. Technol., 42, 265-271, 2005.

[30]. Wang, Y., Chen, N., Wei, W., Cui, J. and Wei, Z., Enhanced adsorption of fluoride from aqueous solution onto nanosized hydroxyapatite by low-molecular-weight organic asid. Desalination, 276, 161-168, 2011.

[31]. Mourabet, M., El Boujaady, H., El Rhilassi, A., Ramadane, H., Bennani-Ziatni, M., El Hamri, R. and Taitai, A., Defluoridation of water using brushite. Dasalination, 278, 1-9, 2011.

[32]. Dou, X., Zhang, Y., Wang, H., Wang, T. and Wang, Y. , Performance of granular Zirconium-iron oxide in the removal of fluoride from drinking water. Water Res., 45, 3571-3578, 2011.

[33]. Lavecchia, R., Medici, F., Piga, L., Rinaldi, G. and Zuorro, A. (2012), Fluoride removal from water by adsorption on a high alumina content bauxite. Chem. Eng. Trans., 26, 225-230.

[34]. Milmile, S.N., Pande, J.V., Karmakar, S., Bonsiwal, A., Chakrabarti, T. and Biniwale, R.B. , Equilibrium isotherm and kinetic modeling of Adsorption of nitrate by anion exchange Indion NSSR resin. Desalination 276, 38-44, 2011.