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Calcium–Zirconium–polyvinyl alcohol polymer composite film as a promising adsorbent for removal of fluoride from aqueous solution

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ABSTRACT

Calcium–Zirconium–polyvinyl alcohol (Ca–Zr–PVA) cross-linked polymer composites were prepared under microwave irradiation and characterized by X-ray fluorescence (XRF), fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) studies. These polymer composites were used as adsorbents for removal of fluoride ions from aqueous solutions. The effects of contact time, solution pH, and adsorbent dose were studied. The adsorption was found to be nearly independent of the pH of the solution and the maximum fluoride adsorption capacity of the adsorbent was 12.72 mg g^{-1}. Langmuir adsorption isotherm fitted better with the experimental data of adsorption equilibrium studies than Freundlich isotherm. The kinetics of the adsorption process indicated second-order uptake of fluoride by the polymer composites. The polymer composites could be considered for the development of a feasible technology for fluoride removal from aqueous solutions.

Keywords: Polymer composite; Adsorption; Fluoride; Kinetics; Isotherm

1. Introduction

Fluorine is highly reactive and is often found in combined states as fluorides [1]. The physiological effects of fluoride on human health include dental, skeletal, and non-skeletal fluorosis [2]. The problem of fluorosis is associated mainly with ground water, which is the primary source of potable water, especially in semi-urban and rural areas in India [3]. When water percolates through fluoride-rich soil, it leaches out fluoride and contaminates the ground water. If the concentration of fluoride in water consistently exceeds the permissible limit of 1.5 mg L^{-1} (as per WHO), then it becomes imperative to consider some remedial measures to check the prevalence of fluorosis [4]. A variety of defluoridation technologies are in practice worldwide, but still the search for a viable technology is on. Adsorption continues to be the most widely used method for defluoridation of water due to its low cost and viability [5–7].

The present study attempts to investigate the role of polymer composites as potential defluoridating agents [8–12]. A judicious choice of the polymer, like PVA which is non-toxic as well as degradable, will facilitate the environmentally safe synthesis [13].

The study is based on a one-pot greener method of synthesis of cross-linked PVA-bimetallic systems using microwave irradiation. These composites are

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particularly remarkable since combining two metals may provide selectivity. Also, some combinations may exhibit synergistic effects [14–16].

2. Experimental

The reagents, $ZrOCl_2·8H_2O$, $Ca(NO_3)_2·4H_2O$, and PVA, used in the study were of analytical grade.

2.1. Synthesis of PVA-cross-linked bimetallic composites

The polymer composites were prepared by mixing 25 mL of 3% wt PVA with 12.5 mL of an aqueous solution of 0.01 mol dm^{-3} $ZrOCl_2·8H_2O$ and 12.5 mL of 0.1 mol dm^{-3} $Ca(NO_3)_2$ in a polyethylene beaker, which was subsequently irradiated with microwaves in a microwave oven at 90 W. The mixture was heated in the open beaker till a cross-linked polymer film was left behind. PVA chains which cross-linked from an aqueous solution at 350 W, cross-linked at just 90 W in the presence of Zr and Ca ions.

2.2. Batch adsorption experiments

Standard fluoride solutions were prepared by appropriate dilution of 100 mgL^{-1} fluoride stock solution (Orion, 940907) using double-distilled water. Batch type fluoride adsorption experiments were carried out at 29 ± 1℃. The adsorption was investigated at varying pH, adsorbent dose, and contact time. The adsorption isotherms and kinetics were then studied. Fluoride analysis was carried out by a potentiometric method using Orion potentiometer, model 720Aplus with combined fluoride electrode [17].

3. Results and discussion

3.1. Characterization of adsorbent

The polymer composites were characterized by FTIR, XRF, and the surface morphology of the polymer composites was studied by taking its SEM and TEM images. X-ray fluorescence indicated the presence of Ca and Zr in the polymer film, the former in a larger quantity (Fig. 1).

The SEM and TEM micrographs show that the distribution of inorganic particles is relatively uniform in the Ca–Zr–PVA polymer composites (Figs. 2 and 3).

The cross-linking of bimetallic polymer composite is confirmed by the FTIR spectrum of the PVA polymer composite, which is almost the same as that of pure cross-linked PVA. Both spectra have characteristic $C–H_{str}$ at 2,914 and 2,820 cm^{-1} and wide $O–H_{str}$ at 3,428 cm^{-1}. However, the $O–H_{str}$ peak intensity decreases in the spectrum of the PVA polymer composite which can be attributed to the diminished number of surface hydroxyl groups. Stronger peaks in the range 1,090–1,380 cm^{-1} can be assigned to $C–O–C_{str}$ which is due to increased cross-linking reaction of PVA, where Ca and Zr act as chemical cross-linkers among PVA polymer chains (Fig. 4). Appearance of new bands in the lower frequency ranges 470, 690, and 850 cm^{-1} can be associated with M–O–C absorptions (M = Ca and Zr).

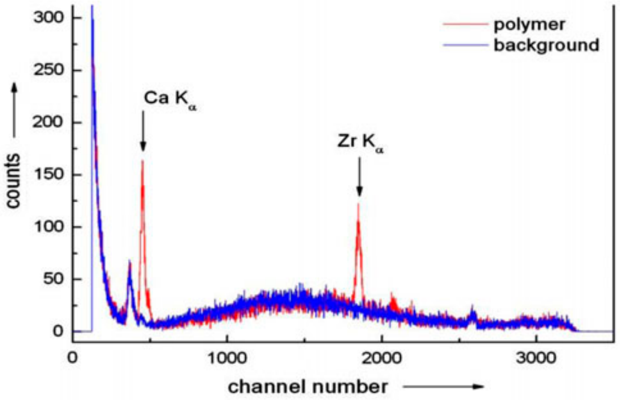

Fig. 1. X-ray spectrum of Ca–Zr–PVA polymer composite.

Initially, the hydroxyl groups of PVA probably couple with metal ions giving polymer–metal ion complex. In the presence of microwave irradiation, a successive reduction of two metal ions occurs. The metal ion of higher reduction potential, Zr^{4+}, is reduced first, and subsequently, Ca^{2+}. Zirconium metal atoms which are more weakly coordinated with the polymer, form aggregates, which in turn coordinate with the stabilizing PVA. The Ca atoms also exhibit a similar pattern [14].

When the polymer composites were synthesized by taking progressively increasing volume ratios of the reactants mixed in the concentration 3% by wt PVA, 0.1 mol dm^{-3} Ca^{2+},and 0.01 mol dm^{-3} Zr^{4+}, the fluoride uptake capacity of the adsorbent was found to increase drastically (Table 1).

The fluoride adsorption capacity of pure cross-linked PVA was found to be 32%, whereas that of Ca–Zr–PVA polymer composite taken in the volume ratio of 12.5:12.5:25 was as high as 97.14%. Zirconium forms a very stable complex with fluoride, as it has high affinity for it in comparison with calcium [5]. These polymer composites are particularly remarkable as adsorbents since the presence of the two metals as inorganic hosts provides selectivity, and also exhibits synergistic effect. The polymer films also have larger surface area making them good adsorbents. Hence, Ca–Zr–PVA bimetallic polymer composites synthesized in the volume ratio of 12.5:12.5:25 were selected for equilibrium and adsorption studies.

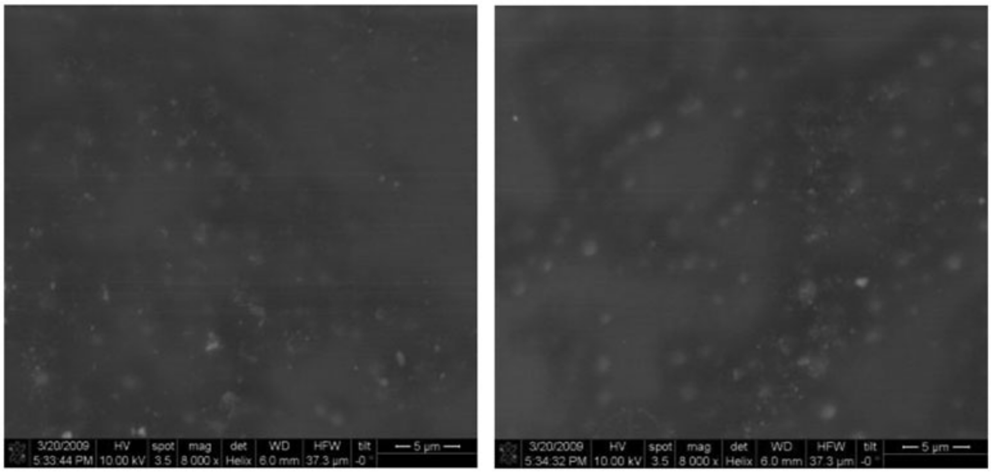

Fig. 2. SEM images of Ca–Zr–PVA polymer composite.

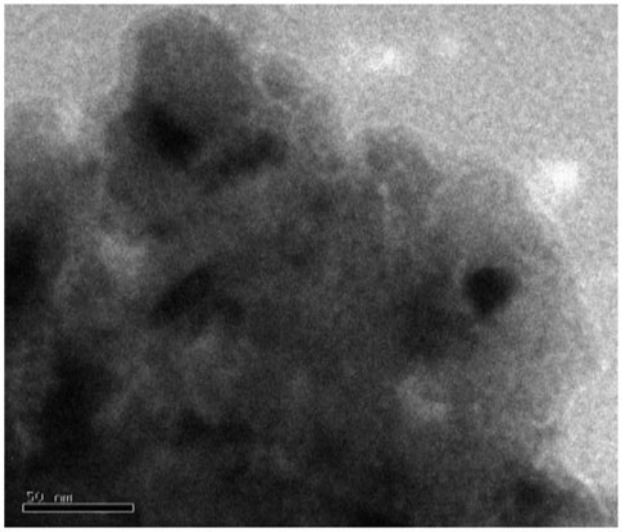

Fig. 3. TEM image of Ca–Zr–PVA polymer composite.

3.2. Effect of pH

As pH controls the adsorption at the solvent–adsorbent interface, the effect of pH on fluoride adsorption capacity of the polymer composite was studied with 25 mL of 5 $\mathrm{mgL^{-1}}$ of fluoride test solutions, which were adjusted to pH 4, 7, and 9 by adding the required amounts of 0.1 $\mathrm{mol\,dm^{-3}}$ HCl and 0.1 $\mathrm{mol\,dm^{-3}}$ NaOH. The fluoride sorption by the polymer composites was found to be nearly independent of pH (Table 2). Therefore, further experiments were carried out at neutral pH.

3.3. Effect of adsorbent dose

The fluoride uptake capacity of the adsorbent steadily increased when the dosage increased from 0.15 to 0.51 g (Fig. 5). This rise might have been due to the increase in surface area or adsorption sites of the adsorbent. However, beyond 0.51 g, the capacity remained practically unchanged and steady. Thus, the optimum dose of the adsorbent can be assumed to be 0.51 g/25 mL.

3.4. Adsorption equilibrium studies

The adsorption isotherms for fluoride uptake on one gram of PVA composite were studied at various fluoride concentrations. The suspensions were shaken for one hour on a mechanical shaker and left to equilibrate for two hours. Equilibrium studies were carried out in order to determine the conditions for maximum fluoride removal by PVA composite. The adsorption capacity reached an equilibrium value after 3 h of contact time. Beyond this, there was negligible change in the residual fluoride concentration.

The equilibrium of the adsorption process for the distribution of fluoride between the liquid and the solid phase can be expressed by the widely used Freundlich and Langmuir models. The Freundlich isotherm, which is generally used for heterogeneous surface systems, is given by the following linearized equation [18]:

$$\log q_{\mathrm{e}} = \log k + \frac{1}{n}\log C_{\mathrm{e}} \tag{1}$$

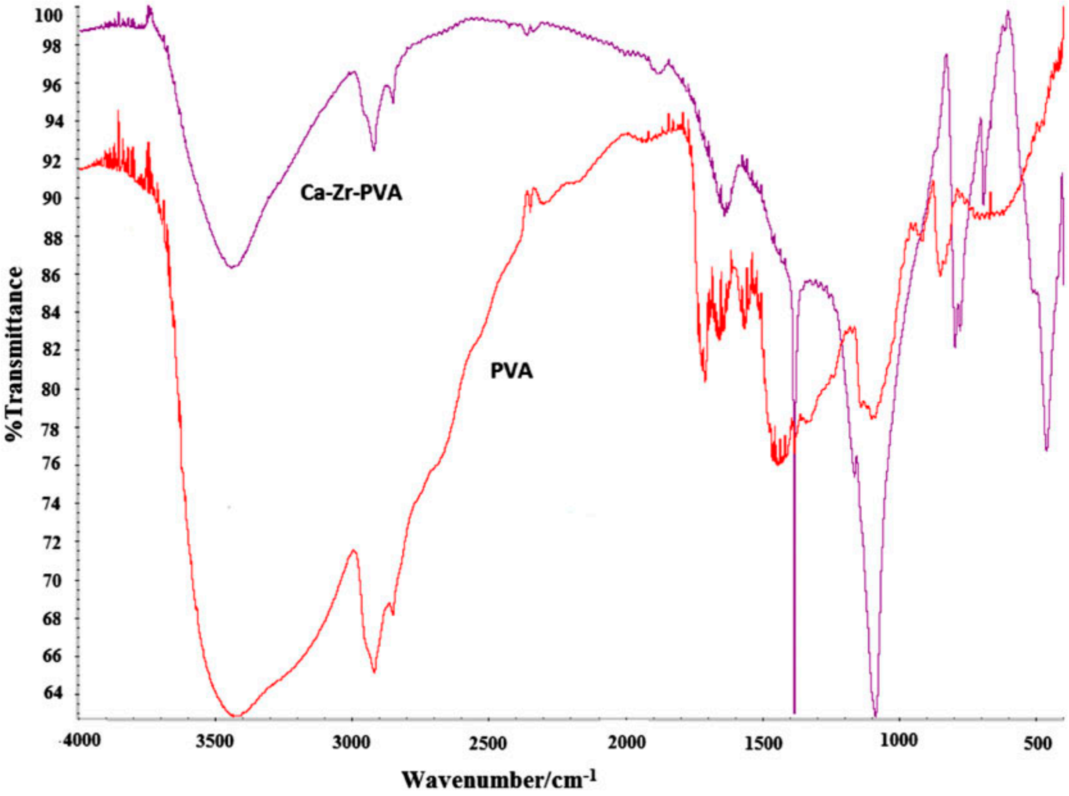

Fig. 4. FTIR spectrum of cross-linked PVA and Ca–Zr–PVA polymer composite.

Table 1
Variation of percent adsorption of fluoride with adsorbent dosage

S. No.	PVA–Ca–Zr volume ratio (mL)	wt. of adsorbent (g)	Fluoride adsorption (%)
1	4:02:02	0.17	73.00
2	8:04:04	0.32	76.40
3	12:06:06	0.52	89.86
4	25:12.5:12.5	1.10	97.14

Notes: Contact time = 2 h, initial fluoride concentration = 5 mgL^{-1}, and volume of solution = 25 mL.

Table 2
Effect of pH on fluoride sorption by the Ca–Zr–PVA polymer composite

pH	wt. (g)	Fluoride adsorption (%)
4	1.13	97.20
7	1.13	97.02
9	1.13	97.30

Notes: Contact time = 2 h, initial fluoride concentration = 5 mgL^{-1}, and volume of solution = 25 mL.

where q_e is the amount of fluoride adsorbed per unit mass of the adsorbent, C_e is the concentration of fluoride at equilibrium, and k and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The value of k is 1.649 mg g^{-1} and $1/n$ is 0.5407 for Freundlich isotherm. The study reveals favorable adsorption by the polymer composite since $1/n$ is less than unity. The correlation coefficient value (R^2) for the isotherm is 0.941, which confirms the validity of the equation for the polymer composite system (Fig. 6).

The Langmuir model is valid for a monolayer adsorption on the surface with a finite number of identical sites. Langmuir linearized equation is usually applied to compute adsorption capacity and is given as [19],

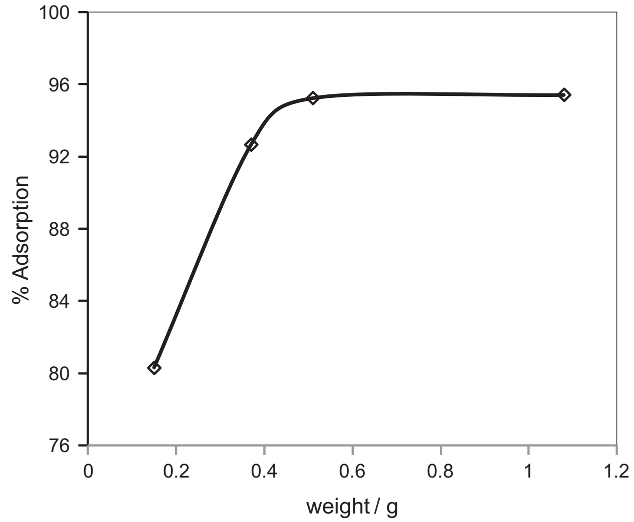

Fig. 5. Effect of adsorbent dosage on fluoride removal. Contact time = 2 h, initial fluoride concentration = 5 mgL^{-1}, and volume of solution = 25 mL.

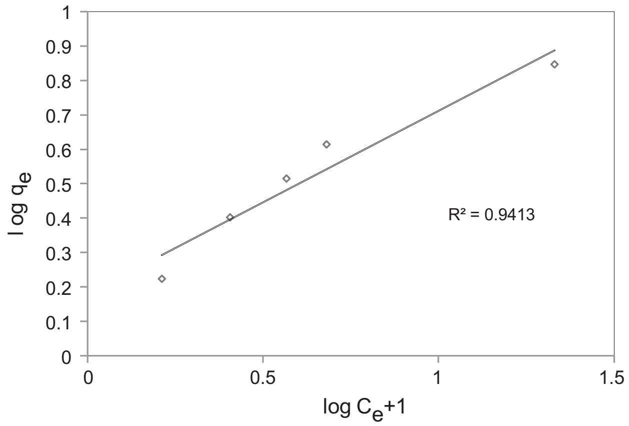

Fig. 6. Freundlich adsorption isotherm for Ca–Zr–PVA polymer composite. Contact time = 3 h, initial fluoride concentration = 5 mgL^{-1}, volume of the solution = 100 mL, and adsorbent dose = 1.0 g.

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_0 b}\frac{1}{C_e} \tag{2}$$

q_e is the amount of fluoride adsorbed per unit weight of the adsorbent (mg g^{-1}) on attainment of equilibrium, q_0 is the maximum sorption capacity corresponding to complete monolayer coverage (mg g^{-1}), and C_e is the equilibrium fluoride concentration (mg L^{-1}). Langmuir constant b, which is indirectly related to the energy of adsorption is associated with the affinity of the binding sites.

The values of Langmuir parameters are $q_0 = 12.72$ mg g^{-1} and $b = 1.058$ L mg^{-1}. In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter r was determined using the following equation:

$$r = \frac{1}{1 + bC_0} \tag{3}$$

Generally, values of $r < 1$ represent favorable adsorption. In this case, r was found to be 0.158 for the initial fluoride concentration of 5 mgL^{-1}, which confirms that the ongoing adsorption is favorable. The correlation coefficient value (R^2) for Langmuir model is 0.995. Hence, defluoridation brought about by PVA composites in the experiment fits well with the Langmuir adsorption isotherm, suggesting a chemical interaction of fluoride ions with the adsorbent (Fig. 7). The free energy change for adsorption is −2.83 kJ mol^{-1}, indicating that the adsorption of fluoride on the adsorbent is a spontaneous process.

3.5. Adsorption kinetic studies

The effect of contact time was studied with one gram of adsorbent added to 100 mL of 5 mgL^{-1} standard fluoride solution at 29˚C. The fluoride concentration was analyzed at selected time intervals using fluoride ion-selective electrode. The adsorption of fluoride was rapid during the first 60 min, after which the rate slowed down as it approached equilibrium

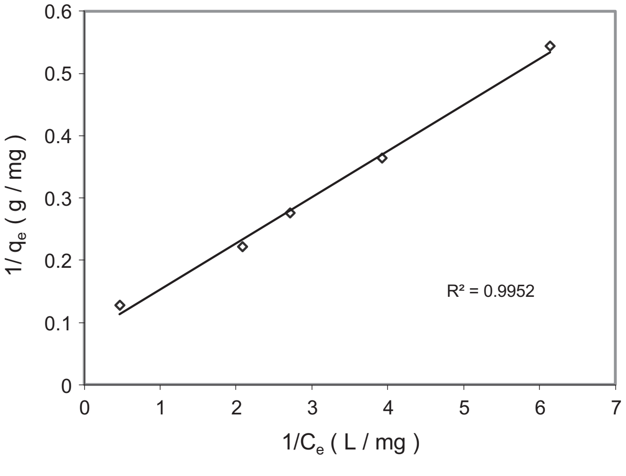

Fig. 7. Langmuir adsorption isotherm for Ca–Zr–PVA polymer composite. Contact time = 3 h, initial fluoride concentration = 5 mgL^{-1}, volume of the solution = 100 mL, and adsorbent dose = 1.0 g.

(Fig. 8). Kinetics of adsorption describes the solute uptake rate, which is one of the important characteristics defining the efficiency of adsorption. Therefore, the kinetic data were fitted to pseudo-first-order and pseudo-second-order kinetic models to arrive at the mechanism of adsorption.

The adsorption rate constants (k_1 and k_2) for the adsorption process were determined from the following integrated rate law equations [20–22]:

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

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

q_e is the amount of fluoride adsorbed per unit mass of PVA composite (mg g^{-1}) at equilibrium, q is the amount of fluoride adsorbed per unit mass (mg g^{-1}) of PVA composite at time t, and k_1 and k_2 are the rate constants of the first-order and second-order reactions, respectively. The value of the first-order rate constant k_1 was calculated from the slope of the linear plot of log(q_e–q) vs. time and was found to be 0.0122 min^{-1} for the initial fluoride concentration of 5 mgL^{-1} (Fig. 9). The value of second-order rate constant k_2 was calculated from the intercept of linear plot of t/q vs. t which was found to be 0.0222 g mg^{-1} min^{-1} (Fig. 10). The kinetics indicates that the fluoride adsorption on the polymer composite obeys the pseudo-second-order kinetic model (R^2 = 1) better than the pseudo-first-order kinetic model (R^2 = 0.977), which suggests that a chemisorption process is involved. The rate of adsorption should be proportional to the second power of fluoride for strict surface adsorption.

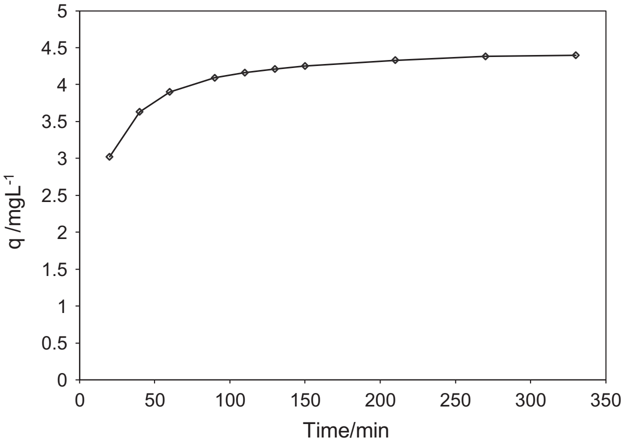

Fig. 8. Effect of contact time for fluoride removal by Ca–Zr–PVA polymer composite. Initial fluoride concentration = 5 mgL^{-1}, volume of the solution = 100 mL, and adsorbent dose = 1.0 g.

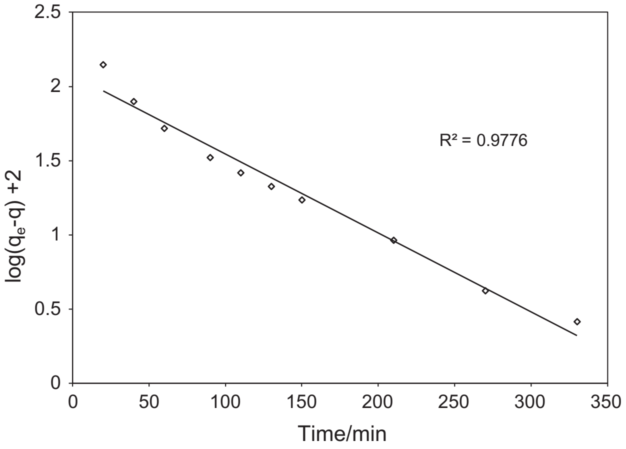

Fig. 9. Pseudo-first-order kinetics of fluoride sorption by Ca–Zr–PVA polymer composite.

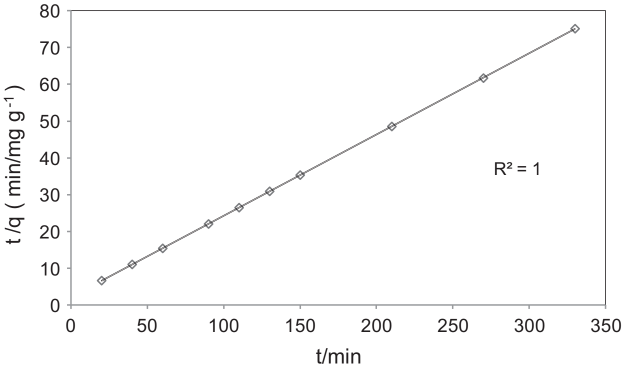

Fig. 10. Pseudo-second-order kinetics of fluoride sorption by Ca–Zr–PVA polymer composite.

4. Conclusions

Ca–Zr–PVA polymer composite would prove to be a suitable adsorbent for the defluoridation of water, as it has high affinity for fluoride. Sorption by the polymer composite is found to be independent of the pH of the medium, thereby making it a promising sorbent material for defluoridation. The Langmuir adsorption isotherm fits well with the fluoride adsorption data, confirming surface homogeneity of the adsorbent and the process as monolayer chemical adsorption. The adsorption of fluoride by polymer composite follows a second-order-kinetics. Thus, the equilibrium and kinetic data would be useful to design an appropriate technology for defluoridation.

Acknowledgments

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Nomenclature

b	—	Langmuir constant related to affinity of binding sites
C_e	—	equilibrium concentration of fluoride
C_o	—	initial concentration of fluoride
k	—	Freundlich constant related to adsorption capacity
k_1	—	pseudo-first-order rate constant
k_2	—	pseudo-second-order rate constant
$1/n$	—	adsorption intensity
r	—	dimensionless equilibrium parameter
R^2	—	correlation coefficient
t	—	time
q	—	amount of fluoride adsorbed at time t
q_e	—	amount of fluoride adsorbed at equilibrium
q_0	—	monolayer coverage capacity

References

[1] L. Pauling, The Nature of Chemical Bond, third ed., Cornell University Press, Ithaca, 1960.

[2] N.V.R. Rao, K.S.P. Rao, R.D. Schuling, Fluoride distribution in waters of Nalgonda District, Andhra Pradesh, India, Environ. Geol. 21 (1993) 84–89.

[3] RGNDWM, Prevention and Control of Fluorosis in India. Water Quality and Defluoridation Techniques, vol. 2, Rajiv Gandhi National Drinking water Mission, Ministry of Rural Development, New Delhi, 1993.

[4] WHO, Guide lines for Drinking water Quality, third ed., vol. 1, World Health Organization, Geneva, 2004.

[5] C. Janardhana, G.N. Rao, R.S. Sathish, V.S. Lakshman, Study on defluoridation of drinking water by impregnation of metal ions in activated charcoal, Indian J. Chem. Technol. 13 (2006) 414–416.

[6] R.S. Sathish, N.S.R. Raju, G.S. Raju, G.N. Rao, C. Janardhana, Equilibrium and kinetic studies for fluoride adsorption from water on zirconium impregnated coconut shell carbon, Sep. Sci. Technol. 42 (2007) 769–788.

[7] R.S. Sathish, S. Sairam, V.G. Raja, G.N. Rao, C. Janardhana, Defluoridation of water using zirconium impregnated coconut fiber carbon, Sep. Sci. Technol. 43 (2008) 3676–3694.

[8] M. Karthikeyan, K.K.S. Kumar, K.P. Elango, Batch sorption studies on the removal of fluoride ions from water using eco-friendly conducting polymer/biopolymer composites, Desalination 267 (2011) 49–56.

[9] N. Viswanathan, S. Meenakshi, Synthesis of Zr(IV) entrapped chitosan polymeric matrix for selective fluoride sorption, Colloids Surf., B 72 (2009) 88–93.

[10] P. Miretzky, A.F. Cirelli, Fluoride removal from water by chitosan derivatives and composites: A review, J. Flourine Chem. 132 (2011) 231–240.

[11] M.S. Kondratenko, I.I. Ponomarev, M.O. Gallyamov, D.Y. Razorenov, Y.A. Volkova, E.P. Kharitonova, A.R. Khokhlov, Novel composite Zr/PBI-O-PhT membranes for HT-PEFC applications, Beilstein J. Nanotechnol. 4 (2013) 481–492.

[12] G. Alagumuthu, T.A. Kumar, Synthesis and characterization of Chitosan/TiO_2 nanocomposites using liquid phase deposition technique, Int. J. Nanosci. Nanotechnol. 4 (2013) 105–111.

[13] N.A. Peppas, Y. Huang, M. Torres-Lugo, J.H. Ward, J. Zhang, Physicochemical foundations and structural design of hydrogels in medicine and biology, Annu. Rev. Biomed. Eng. 2 (2000) 9–29.

[14] M.N. Nadagouda, R.S. Varma, Preparation of novel metallic and bimetallic crossed poly(vinyl alcohol) nanocomposite under microwave irradiation, Macromol. Rapid Commun. 28 (2007) 465–472.

[15] R.S. Varma, Advances in Green Chemistry: Chemical Syntheses Using Microwave Irradiation, AstraZeneca Research Foundation India, Bangalore, 2002.

[16] R.S. Varma, Microwave Technology—Chemical Synthesis Applications: Kirk-Othmer Encyclopedia of Chemical Technology, fifth ed., Wiley, New York, NY, 2004.

[17] APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, 1998.

[18] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem. 57 (1906) 385–470.

[19] I. Langmuir, The constitution and the fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[20] S. Azizian, Kinetic models of sorption: A theoretical analysis, J. Colloid Interface Sci. 276 (2004) 47–52.

[21] Y.S. Ho, Citation review of Lagergren kinetic rate equation on adsorption reactions, Scientometrics 59 (2004) 171–177.

[22] Y.S. Ho, Review of second order models for adsorption systems, J. Hazard. Mater. 136 (2006) 681–689.