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Fluoride removal from aqueous solution by pumice: case study on Kuhbonan water

M. Malakootian*, M. Moosazadeh, N. Yousefi, A. Fatehizadeh

School of Public Health, Kerman University of Medical Sciences, Kerman, Iran.

The fluoride removal from synthetic water by pumice was studied at batch experiments in this study. The effect of pH, contact time, fluoride concentration and adsorbent dose on the fluoride sequestration was investigated. The optimum conditions were studied on Kuhbonan water as a case study. The results showed that with increasing of the absorbent amount; contact time and pH improve the efficiency of fluoride removal. The maximum fluoride uptake was obtained in pH and contact time 7.0 and 180 min, respectively. Also, with increasing initial concentration of fluoride in water, the efficiency of fluoride removal decreased. The obtained results in this study were matched with freundlich isotherm and pseudo second order kinetic. The maximum adsorption capacity (Q_m) and constant rate were found 0.31 (mg/g) and 0.21 (mg/g.min), respectively. This study also showed that in the optimum conditions, the fluoride removal efficiency from Kuhbonan water by 2.8 mg/L fluoride was 74.64%. Eventually, pumice is recommended as a suitable and low cost absorbent to fluoride removal from aqueous solutions.

Key words: Adsorption, Freundlich isotherm, Langmuir isotherm, Kuhbonan water.

INTRODUCTION

In natural water, fluorides exist with iron, aluminum and beryllium as fluoride ion (F^-) (Crittenden et al., 2005). Contact with mineral sediments as well as discharge of industrial wastewater containing fluoride is a key contributor to groundwater and surface water pollution (Gupta et al., 2007). According to World Health Organization (WHO) guidelines, the optimum concentration of fluoride in drinking water is 1.5 mg/L (Zhang et al., 2005). Excessive consumption of fluoride for a long term can lead to skeletal damage, dental fluorosis, mental disorders in children, osteosclerosis and structural changes in DNA (Emamjomeh and Sivakumar, 2009). Fluoride removal from water has been performed by chemical precipitation, ion exchange (IE), adsorption, reverse osmosis (RO), electrodialysis (ED), nanofiltration (NF), electrocoagulation (EC), ion exchange membranes and membrane coagulation reactors (MCR) (Crittenden

et al., 2005; Hu et al., 2005; Tahaikta et al., 2007; Zhao et al., 2008). Defluoridation of water by active alumina is similar to ion exchange process, but is much more complex. The disadvantages of active alumina and ion exchange application are disposal of backwash water, regeneration, high detention time, strongly pH dependent and low adsorption capacity (Ku and Chiou, 2002). The key disadvantage of fluoride removal by membrane filtration is disposal of concentrated water (Crittenden et al., 2005).

Adsorption is a mass transfer process which a constituent in the liquid or gas phase is accumulated on solid or liquid phase and separated from its original environment (Crittenden et al., 2005). In water treatment, the adsorption process has been used for removal of taste and odor causing compounds, synthetic organic chemicals (SOCs), colour-forming organics, disinfection byproducts (DBPs), perchlorate, as well as heavy metals (Crittenden et al., 2005; Malakootian et al., 2008; Steinjauser, 2008). Due to more simple design of adsorption unit, lack of sludge production and low investment costs, the adsorption process has more

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*Corresponding author. E-mail: m.malakootian@yahoo.com. Tel: +98 341 320 5074. Fax: +98 341 320 5105.

Table 1. Analysis geology of pumice.

Constituent	Percentage present (%)
SiO_2	61.5
Al_2O_3	15.49
CaO	5.9
MgO	2.65
Fe_2O_3	8.4
K_2O	1.65
LOI (lost of ignition)	1.59

advantages than other methods in removal of pollutants from water and wastewater (Malakootian et al., 2008). Activated carbon, synthetic polymers, silica- based adsorbents, wood ash and soil types are used as adsorbent (Crittenden et al., 2005; Malakootian et al., 2008; Malakootian et al., 2009).

Pumice is a volcanic stone comprised of irregular connected as well as separated cavities and often composed from high amount of silica compounds (69%) than other minerals. Sulfur gases may be confined in these cavities for many years (Maleki and Borghei, 2005). The result of other studies showed that surface structure of pumice has been banded with metal cations which are resistant towards absorbent rinse (Steinjauser, 2008; Maleki and Borghei, 2005). One of the available resources that can be used as the absorbent is pumice. Pumice is present in most of the mountainous regions of Iran such as north west, west, central and south mountains (Maleki and Borghei, 2005).

Kuhbonan, with an eastern longitude of 56º, 17' and northern latitude of 31º, 25', is located 168 Km northwest of Kerman (Iran); its altitude is 1945 m above sea level. Kuhbonan is one of the regions in Iran whose fluoride level has been reported to be between 2.28 and 5.4 mg/L in its water resources (Sadeghkasmaei et al., 2008).

The aim of this study was to find the method for fluoride removal in order to access to available resources and the feasibility of fluoride removal from Kuhbonan city (southeastern Iran) drinking water as case study.

MATERIALS AND METHODS

Instruments and materials

All the chemicals used throughout this study were of analytical grade. All the adsorption experiments were carried out at 25°C and agitation speed 100 rpm. A stock solution of fluoride was obtained by dissolving NaF salt (2.21 g) in distillated water (1000 mL). HCL and NaOH 0.1 N were used in order to adjust samples pH. The fluoride concentration was measured by Hanna C 200 model. All analysis methods had been taken from "standard methods for examination of water and wastewater" (Clesceri et al., 1999).

Preparation of pumice

The pumice used in this study was obtained from Anar mine

(Kerman, Iran). Before batch experiments were performed, the pumice was first milled and rinsed with deionized water for dust removal. Then, the pumice was dried at 105°C for 24 h to reach a constant weight and sieved the particles smaller than 40 mesh were kept for further consideration in the trials without any further treatment. The average chemical composition of pumice was listed in Table 1. This table showed that pumice is primarily a mixture of Si, Al, Ca, Mg and Fe oxides and the SiO_2 content is the highest. (Table 1)

Batch adsorption study

Effect of pH value on fluoride adsorption

The effect of pH on fluoride adsorption was carried out using initial fluoride concentration 7 mg/L onto 20 g/L of pumice at different pH values (4-9). The solution was agitated at 180 min and the residual fluoride in solutions was determined.

Effect of time on fluoride adsorption

The effect of time on fluoride adsorption was studied using initial fluoride concentration 7 mg/L onto 20 g/L of pumice and at neutral pH. The contact time was varied from 30 to 180 min and the amount of fluoride adsorbed determined.

Effect of sorbent dose

The effect of sorbent dose was conducted by shaking of pumice (5, 8, 11, 14, 17 and 20 g) in 1 L of fluoride solution (7 mg/L) at pH: 7 for contact time 180 min.

Effect of initial fluoride concentration

The effect of initial fluoride concentration was performed by adding 20 g/L of pumice onto 1L of fluoride solution (2, 3, 4, 5, 6 and 7 mg/L) at pH: 7 for contact time 180 min.

The adsorption capacity and removal efficiency of fluoride were calculated with the following equations:

$$q_e m = (C_0 - C_e)V$$

$$E_r = [(C_0 - C_e)/C_0] \times 100$$

Fluoride removal from Kuhbonan water

The optimum conditions were tested on Kuhbonan water as a case study. For this purpose, first Kuhbonan water quality was analyzed that the results are presented in Table 2.
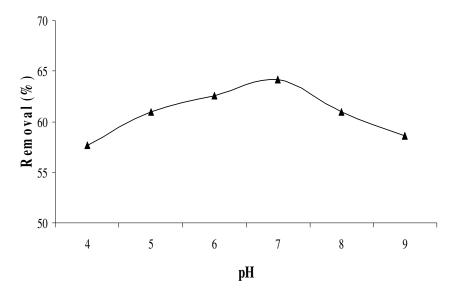
RESULTS AND DISCUSSION

Effect of pH value on fluoride uptake

pH has important role in determining the amount of fluoride adsorbed on the pumice. The results of pH effect on the fluoride removal efficiency are shown in Figure 1. With increasing pH from 4 to 7, the fluoride removal

Table 2. Results of Kuhbonan water analysis.

Parameter	Value (mg/L)
NO_3^-	5.2 ± 0.9
SO_4^{2-}	139 ± 12.3
Cl^-	120 ± 10.2
Alkalinity	200 ± 15.2
Total hardness	450 ± 29.4
TDS	665 ± 43.5
F^-	2.8 ± 0.8
pH	7.5 ± 0.5

Figure 1. Effect of pH on removal efficiency(7 mg/L fluoride, 20 g/L sorbent and contact time 180 min).

efficiency increased from 57.71 to 64.14%. This can be attributed to the formation of weakly ionized hydrofluoric acid in acidic conditions. The correlation coefficient between pH and fluoride removal efficiency was statistically significant (P value = 0.002). The results of this study show an agreement with fluoride removal studies on montmorillonite (pH=6) (Tor, 2006), carbon slurry (about pH 7) (Gupta et al., 2007) and mixed rare earth oxides (about pH 6.5) (Raichur and Basu, 2001).

Effect of contact time on fluoride adsorption

The influence of contact time on the fluoride removal efficiency is shown in Figure 2. It was observed that with a constant dose of pumice, the amount of fluoride adsorbed increases with time up to reach a steady state in 180 min. Correlation coefficient between contact time and fluoride removal efficiency was statistically insignificant (P value = 0.067).
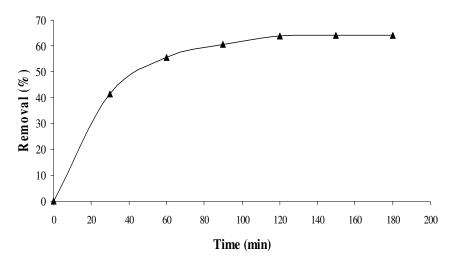
Effect of sorbent dose

The effect of the amount of pumice on fluoride adsorption is shown in Figure 3. Our finding presented that with increase the amount of pumice, the fluoride removal efficiency increases. When the amount of the pumice was increased from 5 to 20 g/L, the fluoride removal efficiency increased from 27.14 to 64.14%. The coefficient of correlation between the amount of pumice and fluoride removal efficiency was statistically significant (P value = 0.028).
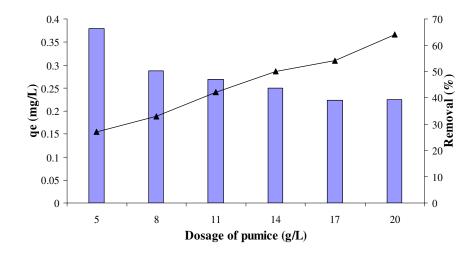
Effect of initial fluoride concentration

The influence of initial fluoride concentration on the fluoride removal efficiency is illustrated in Figure 4. The results showed that fluoride removal efficiency is reduced with increasing the initial concentration of fluoride.

However, the adsorption capacity rose with increasing

Figure 2. Effect of contact time on removal efficiency (7mg/L fluoride, 20g/L sorbent and neutral pH).

Figure 3. Effect of sorbent amount on removal efficiency (contact time 180 min, 7 mg/L fluoride and neutral pH).

the initial fluoride concentration (mg/g) due to a raise in the driving force of the concentration gradient. The fluoride removal efficiency was declined from 85.75 to 64.14% in fluoride concentration from 2 to 7 mg/L. The correlation coefficient between initial concentration of fluoride and fluoride removal efficiency was statistically significant (P value = 0.040). This study have been confirmed with a study on fluoride removal with MgAl-CO$_3$ (Lv et al., 2007).

Fluoride removal from Kuhbonan water

Under obtained optimum conditions in this study (contact time 180 min, actual pH of water and 20 g/L pumice), fluoride removal efficiency from Kuhbonan drinking water

with fluoride concentration 2.8 mg/L was 74.64% (Figure 5). Hence, the residual fluoride in Kuhbonan drinking water is 0.71 mg/L that is less than WHO guidelines.

Isotherm data analysis

In this study, Freundlich (1906), Langmuir 1, 2 (Nemr, 2009) and Temkin (Temkin and Pyzhev, 1940) isotherms were studied. The Table 3 gives the isotherms equation as well as constants. According to the results, the Freundlich isotherm was best fitted to represent the equilibrium adsorption data than other isotherms (Figure 6).

R$_L$ (separation factor) is the important factor in Langmuir isotherm that is the dimensionless constant

Figure 4. Effect of initial fluoride concentration on the removal efficiency(contact time 180min, 20g/L sorbent and neutral pH).
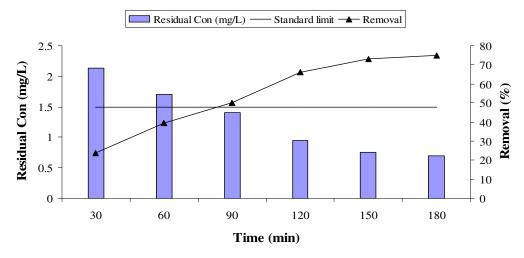

Figure 5. Fluoride removal from Kuhbonan water.

and is defined by following equation (Kumar et al., 2009, Salim and Munekage, 2009);

$$R_L = \frac{1}{1 + bC_0}$$

R_L can be interpreted according to Table 4. Calculated R_L in Langmuir-2 isotherm was 0.13, which indicates that the isotherm was favorable.

Kinetic studies

Fluoride removal from aqueous solution by pumice may be presented by first–order (Nemr, 2009), second-order (Azizian, 2004), Elovich and Intraparticle diffusion kinetic models (Nemr, 2009). Table 5 presents the kinetics equation and constant value for fluoride adsorption on pumice. Fluoride–pumice interaction concurred showed good fit with pseudo-second order rate equation (R^2=0.99). Figure 7 is shown pseudo-second order kinetic model.

Conclusions

Based on these results, the following conclusion can be taken:

1. With increasing of absorbent dose; contact time and pH, the efficiency of fluoride removal increased. Also,

Table 3. The results of isotherms calculation.

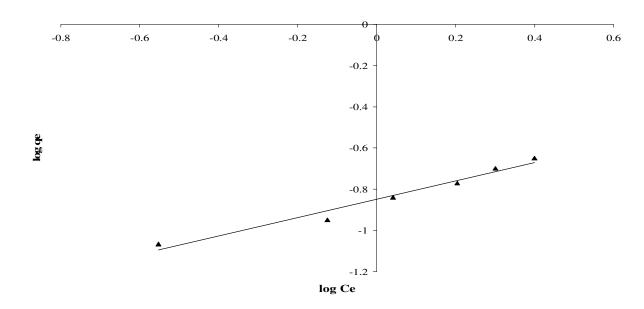| Isotherm	Equation	Liner form	R^2	Constant	Value
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	$\log q_e = \log K_f + \left(\frac{1}{n}\right)\log C_e$	0.97	K_f	0.85
				n	2.45
Langmuir-1		$\frac{C_e}{q_e} = \left(\frac{1}{K_L Q_m}\right) + \left(\frac{1}{Q_m}\right)C_e$	0.93	K_L	0.97
				Q_m	0.31
	$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$				
Langmuir-2		$\frac{1}{q_e} = \frac{1}{Q_m} + \left(\frac{1}{K_L Q_m}\right)\frac{1}{C_e}$	0.89	K_L	2.12
				Q_m	0.22
Temkin	$q_e = \frac{RT}{b_T} Ln(A_T C_e)$	$q_e = B_T \ln A_T + B_T \ln Ce$	0.92	A_T	12.6

Figure 6. Plot of freundlich isotherm for fluoride absorption on pumice at pH 7.0.

Table 4. Separation factor for shape of isotherm.

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favorable

with increasing initial fluoride concentration, the efficiency of fluoride removal decreased. The maximum fluoride efficiency was obtained 85.75% in neutral pH, the contact time of 180 min, 20 mg/L pumice and 2 mg/L initial concentration of fluoride.

2. In this study, Freundlich, Langmuir 1, 2 and Temkin isotherms were studied. The Freundlich isotherm ($R^2 = 0.94$) was best fitted to represent the equilibrium adsorption data than other isotherms.

3. Calculated R_L in Langmuir-2 isotherm was 0.13, which indicates that the isotherm was favorable.

4. Fluoride–pumice interaction concurred was best fitted with pseudo-second order ($R^2 = 0.99$).

5. According to previous studies on fluoride removal from water (Ku and Chiou, 2002), the pumice is a low cost and available adsorbent to removal of fluoride from aqueous

Table 1. Comparison of first and second-order, Elovich and interparticle diffusion kinetic constants.

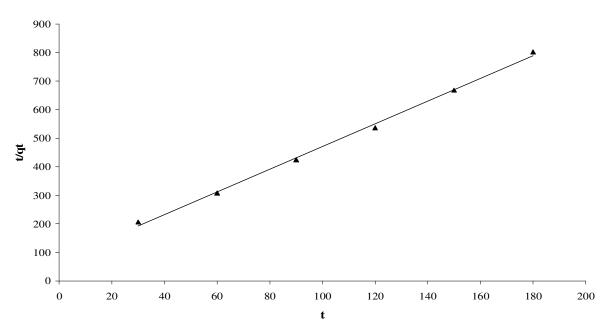| Kinetic	Equation	Liner form	R^2	Constant	Value
Pseudo first order	$\dfrac{dq_t}{dt}=k_1(q_e-q_t)$	$\log(q_e-q_t)=\log(q_e)-\dfrac{k_1}{2.303}t$	0.93	k_1	0.05
				q_e (calc)	0.43
Pseudo second order	$\dfrac{dq_t}{dt}=k_2(q_e-q_t)^2$	$\dfrac{t}{q_t}=\left(\dfrac{1}{k_2q_e^2}\right)+\left(\dfrac{1}{q_e}\right)t$	0.99	k_2	0.21
				q_e (calc)	0.25
Elovich	$\dfrac{dq_t}{dt}=\alpha\exp(-\beta q_t)$	$q_e=\left(\dfrac{1}{\beta}\right)\ln(\alpha\beta)+\left(\dfrac{1}{\beta}\right)\ln t$	0.92	α	0.05
				β	22.22
Interparticle diffusion	-	$q_t=K_{dif}t^{0.5}+C$	0.83	K_{dif}	0.01

Figure 7. Plot of second order model for fluoride absorption onto pumice at pH 7.0

solution.

NOMENCLATURE

C_0: Initial concentration (mg/L)
C_e: Equilibrium concentration in solution (mg/L)
C_t: Equilibrium concentration in solution at time t (mg/L)
k_1: Pseudo first-order rate constant (1/min)
k_2: Pseudo second-order rate constant (g/mg min)
K_{dif}: Intraparticle diffusion rate constant (mg/g min$^{0.5}$)
K_f: Freundlich isotherm constants (L/g)
K_L: Langmuir isotherm constants (L/mg)

n: Adsorption intensity

q_e: Equilibrium adsorbent concentration on adsorbent (mg/g)

q_e cal: Calculated values of q_e (mg/g)

Q_m: Maximum monolayer capacity (mg/g)

q_t: Adsorbed metal concentration at time t (mg/g)

R^2: Correlation coefficients

R_L: Dimensional separation factor

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