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Evaluating the Effectiveness of Modified Pumice in Fluoride Removal from Water

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An excess amount of fluoride ions in drinking water has been known to cause adverse effects on human health. The fluoride removal from synthetic water by modified pumice was studied at batch experiments. The chemical activation process was achieved chemically with $FeCl_3$, $Al_2(SO_4)_3$ and HDTMA-Br. The effect of pH, contact time, fluoride concentration and adsorbent dose on fluoride sequestration was investigated. The results showed that 0.3M HDTMA-Br had best function for pumice modification in fluoride removal. Kinetic data showed that fluoride adsorption was rapid in the beginning and maximum uptake occurred in 0.5 h and equilibrium reached within 3 h. The maximum fluoride adsorption was obtained at pH = 7. Also, with increasing fluoride initial concentration and decreasing pumice dose, the fluoride removal efficiency decreased. The obtained results in this study were matched with Freundlich isotherm and pseudo second order kinetic. The maximum adsorption capacity (q_m) and rate constant were found 0.29 (mg/g) and 0.13 (mg/g min), respectively.

Key Words: Modified pumice, Adsorption model, Kinetic model, Adsorption capacity, Fluorosis.

INTRODUCTION

Contact with mineral sediments and discharge of industrial wastewater containing high fluoride concentrations such as aluminum smelters and coal fired power stations are contributing to entry fluoride to the environment[1]. In natural water, fluoride presents in combination with iron, aluminum and beryllium as fluoride ion[2,3]. It is known that its low concentration as well as its excess causes health problems to the human beings. Fluoride at low concentration is beneficial in dental protection and skeletal damages and its excessive intake led to various disorders and diseases such as crippling skeletal fluorosis, brittle bones, dental fluorosis and change in DNA structure[4,5]. The standard concentration of fluoride ion in drinking water has been reported to be 1.5 mg/L by WHO and 4 mg/L by USEPA[5,6].

There are several techniques for the fluoride removal from water sources such as using chemical precipitation, ion exchange, absorption, reverse osmosis (RO), electrodialysis (ED), nanofiltration (NF), electrocoagulation (EC), ion exchange membranes and membrane coagulation reactors (MCR)[6-10].

Adsorption is an excellent technology, in which fluoride is concentrated onto adsorbent mass. Activated alumina, amorphous alumina, activated carbon, clay, zeolite, calcite, charcoal and red mud goethite, kaolinite have been studied to fluoride removal[11-14]. The aim of this study is to investigate the effect of pumice as absorbent in fluoride removal from aqueous solution.

EXPERIMENTAL

Adsorbent preparation: This research used natural pumice which is originated from Anar (Iran). The average chemical compositions of the pumice are used in this work (weight %) was: 61.5 % SiO_2; 15.9 % Al_2O_3; 5.9 % CaO; 2.65 % MgO; 8.4 % Fe_2O_3; 1.65 % K_2O and 1.59 % LOI (lost of ignition). The chemical activation process was achieved chemically with $FeCl_3$, $Al_2(SO_4)_3$ and hexadecyl trimethyl ammonium bromide (HDTMA-Br) (0.1, 0.2 and 0.3 M). The activated pumice samples were washed with distilled water, dried at 105 ºC.

Preparation of fluoride solution: A stock solution of fluoride was obtained by dissolving NaF (2.21 g) in distilled water (1000 mL). HCl and NaOH 0.1N were used in order to adjust samples pH. The fluoride concentration was measured by Hanna C 200 model. Analyses were performed according to the standard methods for examination of water and wastewater[15].

Batch adsorption experiments: Jar apparatus were filled with 7 mg/L of fluoride solution and constant amount of modified pumice (2.0 g) mixed to 100 mL volume. Upon completion of shaking, the samples were withdrawn at 30, 60, 90, 120, 150 and 180 min and their fluoride concentration was measured. In order to determine the effects of different pH on adsorption rate, samples were influenced by standard HCl and NaOH solution and their pH adjusted to 4, 5, 6, 7, 8 and 9. The effect of different initial concentration was investigated by adding 2.0 g/L of modified pumice onto 100 mL of fluoride solution (2, 3, 4, 5, 6 and 7 mg/L), pH value 7 and agitating time 3 h. The effect of sorbent dose was conducted by shaking of pumice (5, 8, 11, 14, 17 and 20 g) with 1000 mL of fluoride solution (7 mg/L) at solution pH (7) and contact time 3 h.

RESULTS AND DISCUSSION

The results (Fig. 1) show the average of 10 modification type of pumice. The results showed that 0.3M HDTMA-Br had best function for pumice modification in fluoride removal. Surfactants especially HDTMA-Br are stable at various pH ranges and high or low ionic strength. Therefore, possibility of degradation of pumice or desorption of surfactant from the surface of pumice is very low[16].

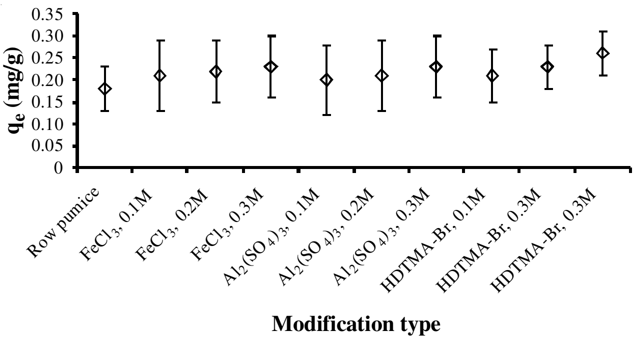

Fig. 1. Effect of various modification methods on pumice

The influence of contact time on the efficiency of fluoride removal is shown in Fig. 2. The result shows as contact time increased, the amount of fluoride adsorbed increases up to reach a steady state value in 3 h. The effect of solution pH on the removal of fluoride during adsorption process is shown in Fig. 3. The maximum fluoride removal was obtained at pH = 7 (73.14 %). This can be attributed to the formation of weakly ionized hydrofluoric acid in acidic conditions[17]. The obtained result in line with carbon slurry (about pH = 7)[1] and mixed rare earth oxides (*ca.* pH = 6.5)[18]. The effect of varying the adsorbent mass on the adsorption of fluoride ions is shown in Fig. 4. The adsorption capacity of fluoride adsorbed per gram of the modified pumice (mg/g) reduced with increasing the dosage of pumice. On the other hand, the removal efficiency of fluoride adsorbed per gram of the pumice (mg/g) increased with the dosage of pumice. The maximum absorption capacity of fluoride was 0.5 (mg/g) at 5 g/L pumice and 7 mg/L fluoride. The feasibility and efficiency of an adsorption process depends not only on the properties of the adsorbents, but also on the concentration of the metal ion solution. The initial metal concentration provides an important driving force to overcome all mass transfer resistances of the metal between aqueous and solid phase[19,20]. Fig. 5 showed the results on effect of fluoride initial concentration. Fluoride removal efficiency fluctuated from 94.75-73.14 %.

Adsorption models: For modeling fluoride adsorption from water, two models (Langmuir and Freundlich) were used: where, q is the amount of metal ions adsorbed per specific amount of adsorbent (mg/g) and C is equilibrium concentration (mg/L or mmol/L); q_m is the amount of metal ions required to form a monolayer (mg/g); K_L is Langmuir equilibrium constant; K_F and n are Freundlich equilibrium constants. These models are useful in full scale applications. As in Figs. 6 and 7 are shown, the adsorption of fluoride is better explained by Freundlich isotherm. Table-1 shows that equation, linear form and constant value of Langmuir and Freundlich isotherms[21,22].

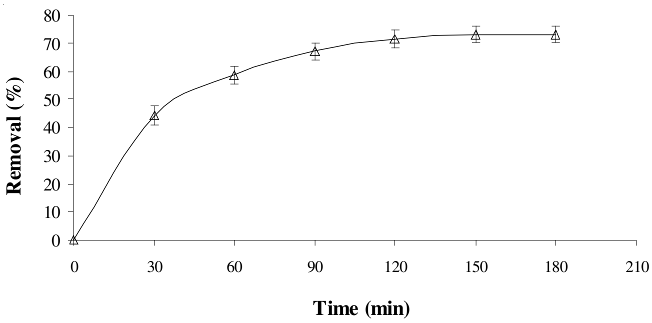

Fig. 2. Effect of contact time on removal efficiency (7 mg/L fluoride, 20 g/L sorbent and neutral pH)

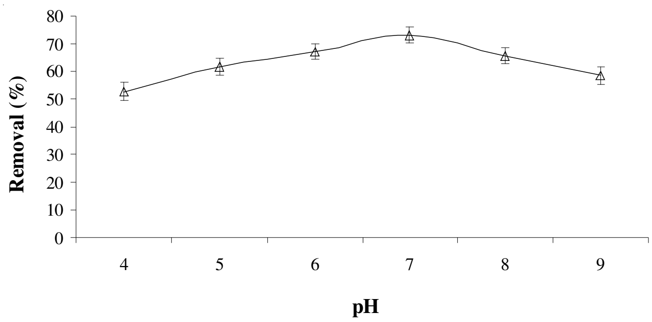

Fig. 3. Effect of pH on removal efficiency (7 mg/L fluoride, 20 g/L sorbent and contact time 3 h)

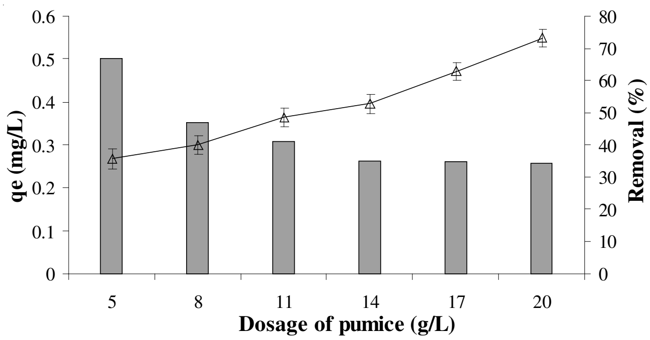

Fig. 4. Effect of sorbent doses on removal efficiency (contact time 3 h, 7 mg/L fluoride and neutral pH)

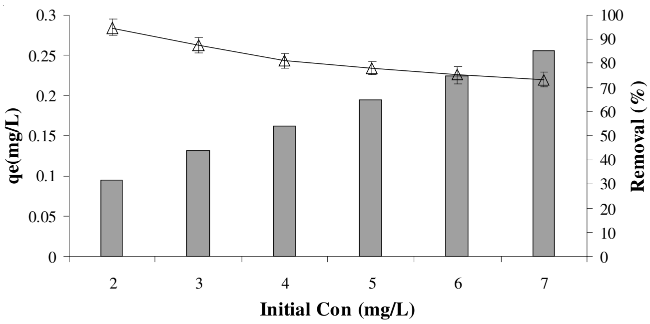

Fig. 5. Effect of initial fluoride concentration on the removal efficiency(contact time 3 h, 20 g/L sorbent and neutral pH)

TABLE-1
FREUNDLICH AND LANGMUIR MODEL (EQUATION, LINEAR FORM AND CONSTANT)

Isotherm	Equation	Linear 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	0.61
				n	2.95
Langmuir	$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \left(\frac{1}{K_L Q_m}\right) + \left(\frac{1}{Q_m}\right)C_e$	0.95	K_L	2.35
				q_m	0.29

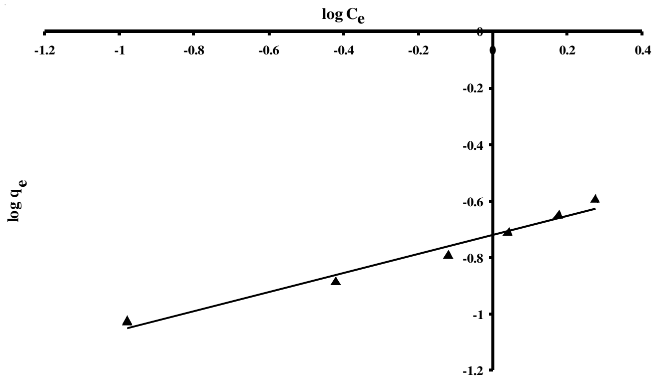

Fig. 6. Freundlich isotherm for fluoride removal by modified pumice, pH = 7

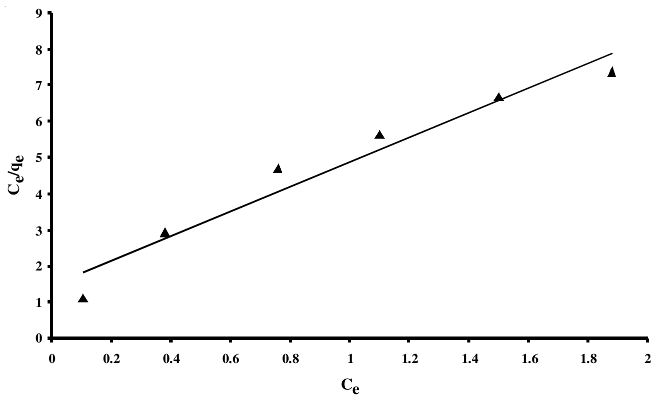

Fig. 7. Langmuir isotherm for fluoride removal by modified pumice, pH = 7

Kinetic models: To find the potential rate-controlling steps involved in the process of adsorption of fluoride onto modified pumice, first order and pseudo second order kinetic models were tested. Adsorption kinetics of fluoride first order and pseudo second order shown in Figs. 8 and 9 and Table-2 which also compared the first order and pseudo second order kinetics constants[23,24].

Conclusion

According to results, the following conclusion are made: (i) HDTMA-Br 0.3 M had best function for pumice modification in fluoride removal. (ii) With increasing adsorbent dose, the removal efficiency increased and the absorption capacity decreased. (iii) The maximum fluoride removal was obtained at pH = 7. (iv) The adsorption of fluoride using modified pumice follows pseudo second order kinetic and better explained by Freundlich isotherm.

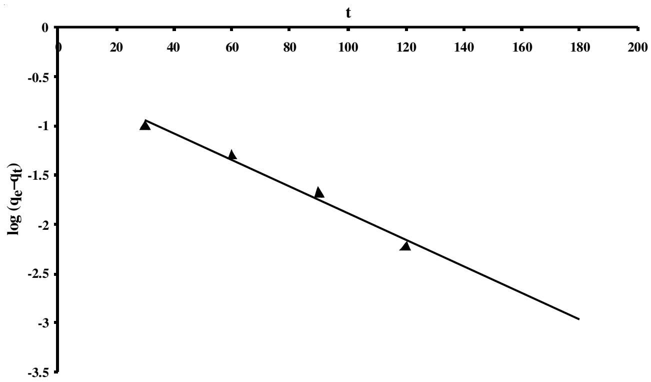

Fig. 8. First order kinetic for fluoride removal

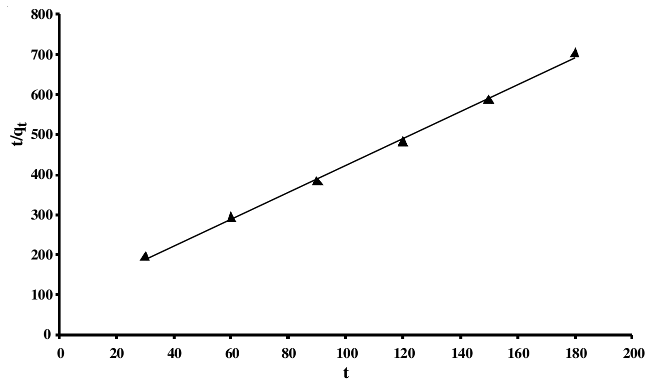

Fig. 9. Pseudo second order kinetic for fluoride removal

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TABLE-2
FIRST ORDER AND PSEUDO SECOND ORDER RATE EQUATION CONSTANTS FOR FLUORIDE REMOVAL BY MODIFIED PUMICE

Kinetic	Equation	Liner form	R^2	Constant	Value
First order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$	0.95	k_1	0.03
				q_e (calcd.)	0.29
Pseudo second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t$	0.99	k_2	0.13
				q_e (calcd.)	0.29

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