Optimization condition of fluoride adsorption using activated clay

Z Mustakin\textsuperscript{1}, F Y Purwaningtyas\textsuperscript{1}, E B Leksono\textsuperscript{1}, Sarto\textsuperscript{2}, and A Prasetya*\textsuperscript{2}  

\textsuperscript{1}Department of Chemical Engineering, Faculty of Engineering, Universitas Muhammadiyah Gresik, Indonesia  
\textsuperscript{2}Department of Chemical Engineering, Faculty of Engineering, University of Gadjah Mada, Yogyakarta, Indonesia  

*Email: aguspras@ugm.ac.id

Abstract. Drinking water which contain high concentration of fluoride can be harmful to teeth and bones. Clay was cleaned from its impurities then treated for 30 minutes at 700 °C and dissolved in HCl solution for 60 minutes. This research focused on the search for process conditions for absorbing fluoride dissolved in water bodies using local material-based adsorption methods using activated clay. The batch sorption experiment was carried out in 50 ml stirred glass container with 1.25 gr, 1 gr, and 1.25 gr of adsorbent weight. The solution samples were analysed by using visible spectrophotometer at 570 nm of the wavelength. From this research, the equilibrium reached in 60 minutes with maximum 78\% fluoride adsorbed. The isotherm models of fluoride removal mechanism fitted well of the Langmuir and Freundlich isotherm models and followed the pseudo second-order kinetics model.

1. Introduction  
Fluoride has potential to contaminate water in areas with metamorphic and granite rock types, which are widely distributed in various regions in Indonesia. Fluoride anion (F\textsuperscript{-}) in the form of organic and inorganic compounds can be found in the surrounding environment [1]. One of the places in Indonesia that has high fluoride concentrations in its body of water is in the crater lake of Ijen in East Java. This high concentration comes from the existing geothermal system in the area. Fluoride concentrations in this area from river water are reported to be 14.2 mg/L, whereas in well water it is reported to be 0.1-4.2 mg/ L [2]. People who live in these areas have potential to be affected fluorosis which affects the health especially the bones, teeth and nervous system.

Fluoride concentrations above threshold levels in groundwater are now a significant environmental health issue because of the negative effects they produce. World Health Organization (WHO) issued a maximum limit of fluoride content in drinking water which is 1.5 mg/L [3, 4]. Dental fluorosis can occur at 1.5-4 mg/L of fluoride concentrations. It is indicated by the presence of white-yellow spots on the teeth and over time turn brown due to excessive fluoride mineralization [5]. Exposure to fluoride with higher concentrations (between 4-10 mg/L) will result in dental and bone fluorosis and at level > 10 mg/L can cause crippling skeletal fluorosis [6, 7]. Fluoride with a high concentration in water and
food that mother consumed during pregnancy/breast feeding can also damage fetus [8]. Other studies show that at low concentrations (0.3-1.2 mg/L) fluoride can work to strengthen tooth enamel [9].

Research on fluoride adsorption have been studied. Removal of fluoride by using clay material with 5-10 g/L of adsorbent dose, pH of 2, and contact time 3 hours obtained 40-50% of removal percentage [10]. China clay has been carried out to removal of fluoride with an initial fluoride concentration of 5.1 mg/L and at temperature 29 °C, an optimum condition of fluoride absorption of 93% was obtained at pH of 3, 1.5 g/100 mL dose of adsorbent, contact time for 2 hours and followed the Freundlich isotherm model [11]. Other studies using bentonite-Al³⁺ clay modification obtained optimum conditions for fluoride adsorption at 60 minutes, 2 mg/100 mL adsorbent dose, and 100 mg/L adsorbate concentration at 26 °C, the isotherm model followed the Langmuir and Freundlich isotherms and the reaction kinetics followed the pseudo second order [12]. Chemically activated kaolin with the addition of sulfuric acid is more effective at absorbing fluoride than unactivated kaolin [13] and pyrophyllite clays which were previously heat treated at 400 °C to remove fluoride from liquid waste compared to raw pyrophyllite have 21% higher adsorption capacity [14].

The rate of fluoride removal was calculated by equation:

\[ \eta = \frac{(C_0 - C_e)}{C_0} \times 100\% \]  

(1)

Where Ce and Co (mg/L) are the equilibrium and initial concentration of fluoride and \( \eta \) is the removal rate (%), respectively. The capacity of adsorption (mg/g) at equilibrium as follows:

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  

(2)

where \( m \) is the adsorbent mass (g) and \( V \) is the volume of the fluoride solution (L). Langmuir and Freundlich isotherms are used to determine the mechanism of fluoride absorption onto adsorbents that can describe the process of adsorption of monolayer and multilayer surfaces [12], respectively. The Langmuir isotherm (Eq. 3) and the Freundlich isotherm (Eq. 4) can be expressed in the form:

\[ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \]  

(3)

\[ q_e = K_F C_e^{1/n} \]  

(4)

where \( q_m \) is Langmuir constants with respect to adsorption capacity (mg/g), \( n \) is intensity of adsorption, \( K_f \) and \( K_L \) are Freundlich constants (L/mg) and Langmuir constants (L/mg), respectively. The adsorption kinetics model was used to determine the estimated of sorption rate and the characteristics of the adsorption mechanism. In this case, the use of pseudo first order (Eq. 5-6) and pseudo second order kinetics (Eq. 7-8) were tested [15, 16]

\[ \frac{dq_t}{dt} = k_1 (q_e - q_t) \]  

(5)

\[ q_t = q_e (1 - e^{-k_1 t}) \]  

(6)

\[ \frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \]  

(7)

\[ q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \]  

(8)

where \( q_e \) and \( q_t \) are the amount of solute that is adsorbed at equilibrium (mg/g) and the amount of solute that is adsorbed on the surface of the adsorbent at any time \( t \) (mg/g), respectively, while \( k_1 \) and \( k_2 \) are the rate constant of first order adsorption (1/min) and second order adsorption (1/min), respectively.
2. Experimental section

2.1. Materials and instrumentation
The material of this research were clay from Kasongan (Yogyakarta), SPADNS Reagent (Merck, CAS 23647-14-5), Zirconyl Chloride Reagent (Merck, CAS 13520-92-8), HCl (Merck, CAS 7647-01-0), NaF (Merck, CAS 7681-49-4), and aquadest. The instrumentations of this research were visible spectrophotometer, sieve shaker, BET surface area analysis, scanning electron microscopy (SEM), X-ray fluorescence (XRF), X-ray diffraction (XRD), shaker water bath, magnetic stirrer, desiccator, filter paper, oven, and beaker glass.

2.2. Procedure
The clay was cleaned by water from its impurities then baked in oven with 120 °C. After drying, it was mashed and sieved with size 100-200 mesh. It baked in furnace for 30 minutes at 700 °C. It saved in desiccator at room temperature. 100 grams of clay was mixed with HCl 1 M solution 1 L by using magnetic stirrer for 60 minutes in beaker glass. It was separated from solution using filter paper and washed until pH was neutral with hot water. It was baked for 4 hours in oven 120 °C then saved in desiccator. It was characterized using XRF, SEM, XRD, and BET to examine its chemical composition, surface topography, structure, and specific surface area, respectively. Activated clay with 0.75 gr, 1 gr and 1.25 gr of weight were mixed with 50 ml of fluoride solution contains concentration 12.17 mg/L and pH of 4. It was shaken in shaker water bath at operating temperature of 25 °C, 35 °C, and 45 °C. The solution samples of fluoride were analyzed by using visible spectrophotometer at 570 nm of the wavelength.

3. Results and discussion

3.1. Characterisation of activated clay
The chemical compositions percentage of activated clay of XRF analysis showed the domination of chemical composition of activated clay were Si (55.58%), Al (21.99%), and Fe (19.58%) component. The alumina content in activated clay determines the amount of fluoride that is absorbed [17]. XRD analysis showed the structure of activated clay and the result are shown in Figure 1(a). XRD patterns indicate that the major crystal phases were Dialuminium silicate oxide (Al₂SiO₅), Barium diiron tetra oxide (BaFe₂O₄), and Cristobalite (SiO₂). Fluoride from wastewater can be removed by Al-O bond structure, which has larger internal specific surface area through specific adsorption. The exchange of ions on activated clay surfaces can be explained by the ligand exchange mechanism. Hydroxyl ions (OH⁻) was replaced by Fluorine ions (F⁻) on the surface of activated clay (Al-OH → Al-F) [14, 18]. Al-F bonds will accumulate on activated clay surfaces until equilibrium is reached. Figure 1(b) shows the scanning electron microscope picture of activated clay. The morphology revealed that the surface structure of activated clay was rough and heterogeneous. The specific surface area of the activated clay was estimated by the BET method and the result was 74.379 m²/g.
3.2. Effect of adsorbent dose

The adsorption capacity for fluoride removal by increasing adsorbent dose are provided in Figure 2. The amount of fluoride adsorbed by the adsorbent will increase with the increasing of adsorbent dose in the same operating time at all temperature operation. It can be understood that the adsorption rate increases with increasing adsorbent dose because an increase in the adsorbent dose will increase the contact (area of adsorption) between the adsorbent and the adsorbate [19]. The equilibrium reached in 60 minutes and the highest yield of fluoride removal (78%) occurred at 45 °C at a dose of 1.25 gr (Figure 3).

![Figure 1. (a) XRD analysis and (b) SEM analysis of activated clay](image)

**Figure 1.** (a) XRD analysis and (b) SEM analysis of activated clay

![Figure 2. Plots for percent fluoride removal at different dose](image)

**Figure 2.** Plots for percent fluoride removal at different dose (a) 25 °C, (b) 35 °C and (c) 45 °C
Figure 3. Plots for percent fluoride removal at different temperature (a) 0.75, (b) 1 and (c) 1.25 gr

3.3. Effect of temperature
The adsorption capacity for fluoride removal by increasing temperature are provided in Figure 3. It showed that with an increase in temperature of the solution 25 °C to 45 °C, the adsorption of fluoride increases from 57% to 66% at 0.75 gr of adsorbent dose, 62% to 74% at 1 gr of adsorbent dose, and 71% to 78% at 1.25 gr of adsorbent dose. The increasing of fluoride removal is due to the more active movement of fluoride molecules with increasing operating temperatures which can touch the surface of the adsorbent faster. It is indicated that the adsorption mechanism of fluoride removal is an endothermic reaction [20].

3.4. Isotherm model
The mechanisms of fluoride adsorption onto activated clay using Langmuir and Freundlich adsorption isotherm models were tested. As shown in Figure 4, both of isotherm models could describe the mechanism of fluoride adsorption well. This indicates that the mechanism of fluoride adsorption occurs by monolayer and multilayer adsorption with the value of regression coefficients ($R^2$) were 0.9774 and 0.9871 of Langmuir and Freundlich adsorption isotherm models, respectively.
3.5. Kinetics model

Figure 5 shows a plot of the kinetic model fit for fluoride adsorption to activated clay with adsorbent dose of 1.25 g/50 ml at 45 °C. This figure shows that the pseudo second-order kinetics model could describe the adsorption mechanism that occurs in fluoride adsorption better than the pseudo first-order kinetics model. The equilibrium reached around 60 minutes with the rate constant of first order sorption and second order were 0.0219 1/min and 0.4697 1/min, respectively.

4. Conclusion

From this research, the maximum removal efficiency of fluoride reached 78% at a dose of 1.25 gr, at 45 °C with time of equilibrium was 60 minutes. The isotherm models of fluoride removal mechanism fitted well of the Langmuir and Freundlich isotherm models and followed the pseudo second-order kinetics model.

References

[1] Habuda-S M, Ravancic M E and Flanagan A 2014 J. Material 7 pp 6317-66.
[2] Heikens A, Sumarti S, Bergen M V, Widianarko B, Fokkert L, Leeuwen K V and Seinen W 2005 Science of The Total Environment 346 pp 56-69.
[3] Hosni K and Srasra E 2011 J. Water Chem. Technol. 33 (3) pp 164-176.
[4] Saikia P, Bharali R J, and Baruah H K 2017 J. Analytical Sci. and Technol. 8 (23).
[5] Dissanayake C B 1991 Int. J. Environ. Stud. 38 137-156.
[6] Valencia-Leal S A, Cortes-Martinez R, and Alfaro-Cuevas-Villanueva R 2012 Int. J. Eng. Research and Develop. 5 (4) pp 69-76.
[7] Ramos-Vargas S, Alfaro-Cuevas-Villanueva R, Huirache-Acuna R and Cortes-Martinez R 2018 *Appl. Sci* **8** 1807.
[8] Rao N 2003 *A Review, in Proceedings of the Third International Conference on Environmental and Health*, pp 386-399.
[9] Dysart A 2008 *Investigation of Defluoridation Options for Rural and Remote Communities, Research Report 41 Salisbury SA 5108*.
[10] Panchore K, Sharma S, Sharma A, and Verma S 2016 *Int. J. Advance Sci. Research* **1** (6) pp 28-32.
[11] Lonare R., Inam F, and Deo S, 2009 *Asian J. Chem.* **23** (1) pp 59-62.
[12] Vhahangwele M, Mugera G W, and Tholiso N 2014 *Toxicol. Environ. Chem.* **96** (9), pp. 1294-1309.
[13] Gogoi P K and Baruah R 2008 *Indian J. Chem. Technol.* **15** (5) pp 500-503.
[14] Kim J H, Lee C G, Park J A, Kang J K, Choi N C, and Kim SB 2013 *Desalin. Water Treat.* **51** pp 3408-3416.
[15] Ho Y S 2006 *Water Research* **40** pp 119-125.
[16] Ho Y S and McKay G 1999 *Process Biochem.* **34** pp 451-465.
[17] Chaturvedi A K, Pathak A K, and Singh V N 1988 *Applied Clay Sci.* **3** pp 337-346.
[18] Gupta N, Gupta V, Singh A P, ang Singh R P 2014 *Bonfring Int. J. Industrial and Management Sci.* **4** (2).
[19] Tripathy S S, Bersillon J L, and Gopal K 2006 *Separation Purification Technol.* **50** pp 310-317.
[20] Abe I, Iwasaki S, Tokimoto T, Kawasaki N, Nakamura T, and Tanada S 2004 *J. Colloid and Interface Sci.* **275** pp 35-39.