



Adsorption and Kinetic Studies for Removal of Fluoride in Aqueous System by Activated Carbon Produced from Lemon Peels

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ABSTRACT: Globally, fluoride contamination in drinking water has been a major environmental problem, imposing severe threat to human health through various disease conditions. Therefore, the objective of this paper was to investigate the adsorption and kinetic studies for the removal of fluoride in aqueous system by activated carbon produced from lemon peels using appropriate standard procedures. Adsorptive efficiency of the lemon peel powder for fluoride ions in water was 94.90% at an optimum contact time of 100 minutes. The fluoride ions removal efficiency of the activated carbon was considered favourable and the data fitted-well to Langmuir and isothermal model with the regression coefficients (R^2) of 0.992 respectively. The adsorption capacity was 0.02 mg/g. From this study, the defluoridation occurs through a chemisorption process when the adsorbent adsorbed fluoride ion from water. The adsorption kinetics studies were best described by pseudo-second order kinetics; the result obtained suggests an endothermic process with a strong regression coefficient (R^2) of 0.998. The adsorbent used exhibited an excellent adsorption capacity due to its internal pore size, wide surface area and chemical nature. These findings reveal that lemon peel powder has the potential to effectively remove fluoride ions from aqueous solution and can be used to provide safe drinking-water.

DOI: <https://dx.doi.org/10.4314/jasem.v28i5.11>

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Cite this Article as: AMAIBI, P. M; EGONG, J. F; IWE, C. R; OBUNWO, C. C. (2024). Adsorption and Kinetic Studies for Removal of Fluoride in Aqueous System by Activated Carbon Produced from Lemon Peels. *J. Appl. Sci. Environ. Manage.* 28 (5) 1413-1419

Dates: Received: 21 February 2024; Revised: 22 March 2024; Accepted: 20 April 2024 Published: 19 May 2024

Keywords: Defluoridation; fluoride ion; adsorption; activated carbon; lemon peels

Fluoride ion is found in drinking water coming either from natural sources like volcanic processes, weathering or from waste water of industries like glass, fertilizer and iron works. Its effect can either be beneficial or detrimental to human health depending on the level of concentration. The beneficial effect includes; bones strengthening and prevention from tooth decay (Tan *et al.*, 2020). The permissible limit of fluoride in drinking-water according to World Health Organization is 1.5mg/L (WHO, 2017). Above this limit fluoride can lead to various diseases such as dental and skeletal fluorosis, brittle bones, cancer, infertility and brain damage (Tan *et al.*, 2020). Fluoride contamination in ground-water has been considered as a major environmental problem; hence, the removal of fluoride ion in water is increasingly

receiving attention in recent years (Mei *et al.*, 2019). Due to the high concentration of fluoride ions found in ground-water, particularly in parts of India, China, Central Africa and South America, it is important, therefore, to find more sustainable methods to effectively remove fluoride ion from water and provide safe drinking water to the growing world population. According to the United Nations Environmental Program (UNEP), about 25 countries in both developed and developing nations are affected by endemic fluorosis (UNEP (1992). Defluoridation techniques can be grouped into three main categories: chemical process, membrane process (nanofiltration, reverse osmosis, and electrodialysis) and adsorption techniques (Azari *et al.*, 2015). Of all the available methods that can be used to remove fluoride from

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aqueous solution, adsorption process simply offers more satisfactory results due to its low cost, high efficiency, reusability and reliability (Ali and Gupta, 2007). Agricultural waste materials contain various organic compounds (hemicelluloses and cellulose and lignin) being responsible for the binding of inorganic contaminants to its surface. On account of these adsorbents to remove contaminants, chemically modified orange peels have enhanced contaminants' adsorption more than unmodified orange peels as reported by Feng *et al.* (2008). These waste materials remain viable adsorbents to contaminants removal because it is more low-cost effective and eco-friendly in nature. In adsorption method, various category of adsorbents are being used for defluoridation studies such as activated alumina, coconut shell carbon, biogases (Abdisa, 2018), chemically activated carbon (Pietrelli, 2005) and other low-cost adsorbent like saw dust (Wang *et al.*, 2009). The activated carbon prepared from rice husk biochar shell has been used for the sorption of dye such as methylene blue (Nworie *et al.*, 2019). In this study, an activated carbon produced from lemon peels was employed to investigate the effects of adsorbent dosage, contact time and the initial fluoride concentration using a batch process. Hence, the objective of this paper was to investigate the adsorption and kinetic studies for the removal of fluoride in aqueous system by activated carbon produced from lemon peels.

MATERIALS AND METHOD

Preparation of lemon peels adsorbent material: Powdered lemon peels were used as adsorbent in this present study. The peels were properly washed with distilled water. It was cut into small pieces and dried under the sun and then in temperature of 120 °C for 5 hours in an oven. About 120 g of the dried biomass was put into a furnace at 450 °C for 2 hours. The formed biochar were removed, ground into powder, sieved, rinsed with double distilled water and finally dried at 60 °C in an air tight oven. Activation of the biochar was done using about 40g of the of the carbonized lemon peel biochar and 1M of 400 mL HNO₃ added in a 1000 mL conical flask with continuous stirring for 1hour. The mixture was diluted with double distill water and decanted several times and then washed with double distill water until the pH was tested to be 7. The activated carbon was then dried in an oven at 110 °C.

Adsorption Studies for Fluoride: Langmuir Isotherm: The linear form of Langmuir model is expressed by equation 1.

$$C_e/q_e = 1/q_m k_1 + \left(\frac{1}{q_m}\right) C_e \quad (1)$$

Where, C_e refers to the equilibrium concentration of fluoride (mg/L) present in the solution, q_e is the amount of fluoride absorbed per unit weight of the adsorbent (mg/g), q_m and k_1 represent the maximum adsorption capacity (mg/g) and the Langmuir constant related to energy of adsorption (L/mg), respectively. Langmuir isotherm is explained in terms of a dimensionless constant separation factor given in equation 2.

$$R_L = \frac{1}{1 + K_L C_0} \quad (2)$$

Where K_L is the Langmuir constant and C_0 is the initial concentration of metal ion. The value of R_L indicates the type of Langmuir isotherm to be irreversible ($R_L=0$), favourable ($0 < R_L < 1$), ($R_L=1$), linear ($R_L > 1$) unfavourable. For this study, all the R_L values for fluoride ions were favourable. Since they are all less than 0 and 1 (Tan *et al.*, 2020).

Freundlich Isotherm: For a single component system, the isotherm is described thus;

$$\frac{C_e}{Q_e} q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

The linear form of the isotherm is;

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

K_F and n in the equation are known as the Freundlich constants, where n gives the favourability of the adsorption technique and K_F is the adsorption capacity. K_F and n can be determined by plotting a graph of $\ln q_e$ versus $\ln C_e$.

Kinetic Model: The kinetics adsorption describes the rate at which the solute is taken by the adsorbent, and this also governs the adsorption reaction time.

Pseudo First Order Rate Equation: This model makes use of Lagergren's rate equation.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

Pseudo Second Order Rate Equation: If the rate of sorption is a second order mechanism the second order kinetic rate equation is expressed as;

$$\frac{Dq_t}{dt} = K(q_e - q_t) \quad (6)$$

Where q_e and q_t are the sorption capacities (mg/g) at equilibrium and at time t , respectively and k is the rate constant of pseudo-second order sorption, g/mg. minutes). For the boundary conditions, $q_t = 0$ to q_t at $t = 0$ to t .

RESULTS AND DISCUSSION

Effect of Adsorbent Dose: Adsorbent dose plays a crucial role for adsorption efficiency. The effect of adsorbent dose was studied by varying the mass of the adsorbent, such as, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 g/L, while keeping other parameters constant at their respective optimum conditions (initial fluoride concentration 1.0 mg/L, PH = 7, contact time 100 minutes, and 200 rpm). The effect of adsorbent dose on removal efficient (%) of the fluoride ion in solution was observed (Figure 1a), the fluoride ion (%) removal shows increase following the adsorbent dose increase. The adsorbent dose involves the extent of surface area available as the active sites for adsorption, which is considered to increase with corresponding increase in fluoride removal efficiency from 79.00 to 92.70% with a decrease in q_e (mg/g). The optimum dosage yields approximately 93% fluoride removal efficiency when maintained at 2.5 g/L. This investigation is consistent with similar studies, which suggests that after a given quantity of adsorbent dose, the fluoride removal cease to increase. This amount is referred to be the optimum dose (Akafu *et al.*, 2019). To achieve 93% fluoride removal efficiency, the adsorbent dose must approach the optimum dose and is found to be 2.5g/L (Fabian *et al.*, 2014; Rafique *et al.*, 2013). Meanwhile, the adsorption capacity of the activated carbon in this study reflects the properties of the adsorbent that can reduce fluoride ion from water. The decrease in amount of fluoride from 0.079 to 0.015 mg/g produce increase in adsorbent dose from 0.5 g/L to 3.0 g/L as observed in the experiment. The adsorbent dose creates more active sites, while the amount of fluoride ion adsorbed becomes fewer per unit mass of the adsorbent. Therefore, as the ratio of amount of fluoride ion to unit mass of the adsorbent decreases, the adsorbent dose increases.

Effect of Contact Time: The contact time is an important parameter to evaluate the performance of the adsorbent capacity. It is the time required for the adsorbent to reach adsorption equilibrium at room temperature (300K). The study of the effect of contact time on fluoride removal was carried out by varying it from 20 to 120 minutes, keeping other parameters constant (at optimum) values (pH = 7, dose of adsorbent 2.5 g/L, and initial concentration of fluoride solution at 1.0 mg/L). The adsorption of fluoride from the aqueous solution according to the contact time ($t < 30$ min) is shown in (Figure 1b). Within the first 40 min, higher amounts of fluoride were adsorbed because the fluoride ions bind rapidly to the available active sites on the surface of the activated carbon instantaneously. Then continued to be adsorbed at a slower rate after 60 minutes. At equilibrium, the removal of fluoride exhibits no increase despite longer

contact time (Tan *et al.*, 2020; Rafique *et al.*, 2013). No considerable change in adsorption after 100 min; this is because the uptake of fluoride after 100 min gradually declines due to diffusion of the ions to enter into inner pores of the porous adsorbent. As the contact time increases, removal efficiency of the adsorbent also increases, of which the reaction time kept at 100 min is for the experiment to be complete, and q_e (mg/g) increases accordingly. A maximum of 94.90% removal could be accomplished by using the activated carbon. Similar patterns were observed for the removal of fluoride by rice husk (Sihag and Pal., 2023).

Effect of Initial Concentration: The effect of initial concentration is one of the major parameters that influence adsorption capacity of an adsorbent. The effect of initial concentration on the extent of removal of the fluoride was studied by varying the concentrations from 1 to 2 mg/L, while keeping other parameters constant (pH = 7, contact time of 100 minutes and dosage at 2.5 g/L). The increase in fluoride concentration yields a decrease in the removal efficiency from 90.20 to 67.45% (Figure 1c). In a previous study, the removal of fluoride efficiency decreases following the increase in initial concentration of fluoride present in solution (Rafique *et al.*, 2013). At fixed quantity of fluoride ion, the maximum adsorption capacity of adsorbent is reached when no considerable active site on the adsorbent is available for adsorption. At low fluoride concentration in solution, more adsorptive sites are available so adsorption occurs more rapidly. While, the fluoride ions at maximum concentration tends to compete with limited active sites at 2.5 g/L of the adsorbent dose to saturate the adsorption sites. The adsorption capacity (q_e) of fluoride ion increased, and the removal efficiency decreased with increase in concentration. The observed results suggest that adsorption efficiency is directly proportional to the initial fluoride concentration in the solution. Therefore, in order to investigate the adsorbent behaviour in the experimental data, it is important to plot the adsorption isotherm model (Figure 2).

Adsorption Isotherm studies: Langmuir Adsorption Isotherm Model: This model accounts for the surface coverage where the rate of adsorption is proportional to the fraction of open area on the adsorbent surface while desorption is proportional to the fraction of the area covered by the adsorbates (Akafu *et al.*, 2019). The straight line graph from the experimental data gives the Langmuir isotherm model presented (Figure 2a). To calculate the maximum adsorption capacity of the adsorbent (q_{max}) and Langmuir constant (K_L), the gradient and the y-intercept obtained from the curve were linearly correlated with R^2 of 0.992 (Table 1). A

dimensionless constant known as the separation factor (R_L) is calculated to further explain the favourability of the adsorption process by the activated carbon. An equation to calculate the R_L is shown in equation 2. The R_L values for adsorption of fluoride on the activated carbon ranged from 0.98 to 0.97. Since, these values were below 1 ($R_L < 1$), the adsorption of fluoride ion on the lemon peel powder is favourable.

Freundlich Adsorption Isotherm Model: The Freundlich isotherm model explains how the adsorbate is retained at non-uniform surface of adsorbent with different adsorption sites because of different adsorption energies also known as uneven multilayer adsorption (Tan *et al.*, 2020). The linearity of this model expresses surface heterogeneity as well as the relative distribution of energy. The linear equation for the Freundlich model results to a gradient with the y-intercept, $y = 0.197x - 1.540$ and is presented in Figure 2b. The equation shows slope (n^{-1}) and the y-intercept were obtained from the graph, which represents intensity of adsorption (n) and relative adsorption

capacity (K_f), respectively (Table 1). The linear regression coefficient (R^2) of the Freundlich isotherm model was 0.934 with an n value = 0.20, indicating less favourable adsorption, since $n < 1$. This value suggests that a weak correlation exist between adsorption capacity of the adsorbent and fluoride ion removed by the adsorbent based on the closeness of R^2 to 1. From the investigation, the removal of fluoride ions from water can best be represented by the Langmuir adsorption isotherm and is in contrast with previously reported studies (Rafique *et al.*, 2013). The heterogeneous surface of the adsorbent allows adsorption to occur with the adsorbate through Vanderwaal forces based on the available sites. To account for adsorption capacity, the rate of adsorption on the surface of adsorbent and desorption can also be compared using Langmuir adsorption isotherm. Langmuir adsorption isotherm model assumes that adsorption would occur when adsorbates form a monolayer on surface of the active sites of the adsorbent without interaction.

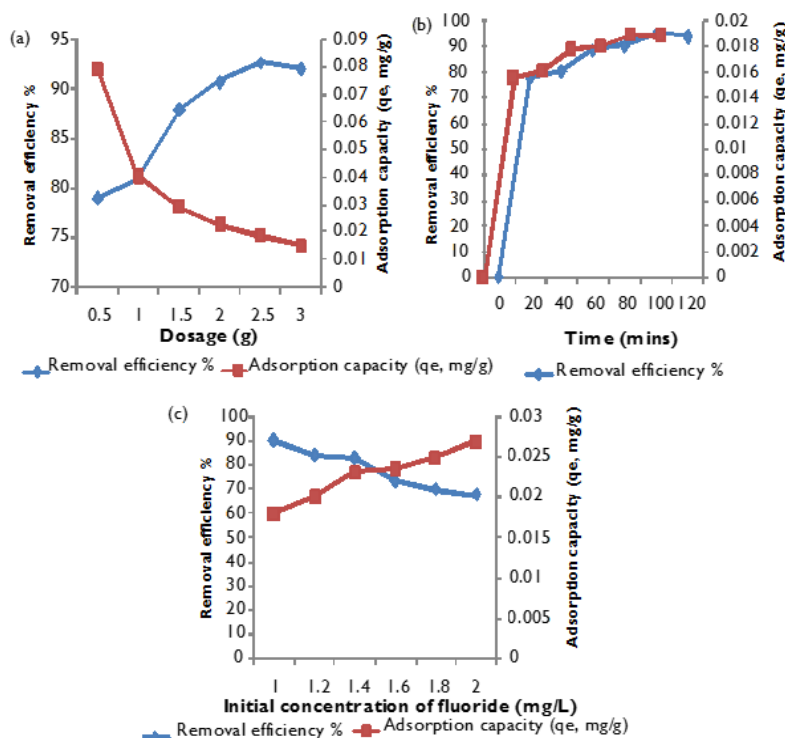


Fig. 1. Percentage Adsorption of Effect of Adsorbent Dosage (a), Time (b) and Concentration (c) on the Fluoride Adsorption Efficiency and Adsorption Capacity Using Lemon Peel Powder as Adsorbent.

Table 1. Comparison of Isothermal Constants for Adsorption of Fluoride

Isotherm Model	Langmuir	Freundlich
	$q_m(\text{mg/g}) = 0.40$	$K_F(\text{mg/g}) (\text{Lmg}^{-1})^{1/n} = 0.21$
	$K_L (\text{L mg}^{-1}) = 0.01$	$n = 0.20$
	$R^2 = 0.992$	$R^2 = 0.934$

Table 2. Kinetic Parameters for Fluoride Adsorption on Lemon Peel Powder

Kinetic model	Experimental data	Pseudo-first-order	Pseudo-second-order
	$q_{e, \text{exp}}(\text{mg/g}) = 0.02$	$q_{e, \text{cal}}(\text{mg/g}) = 1.06 \times 10^{-4}$ $K_1(\text{min}^{-1}) = 0.08$ $R^2 = 0.631$	$q_{e, \text{cal}}(\text{mg/g}) = 0.02$ $K_2(\text{min}^{-1}) = 6.51$ $R^2 = 0.998$

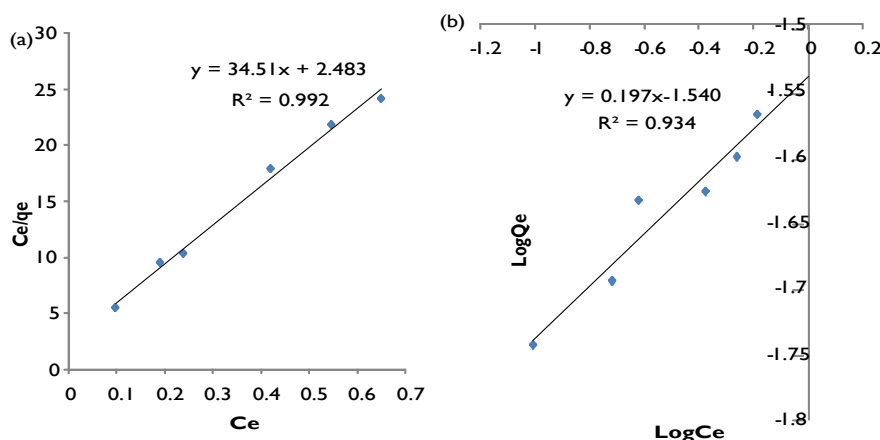


Fig. 2. Adsorption Isothermal of Lemon Peel Powder as (a) Langmuir and (b) Freundlich Isotherms for Fluoride Adsorption. Test conditions: Adsorbent (2.5g/L), Reaction time (100 min) and Fluoride Solution (50 ml).

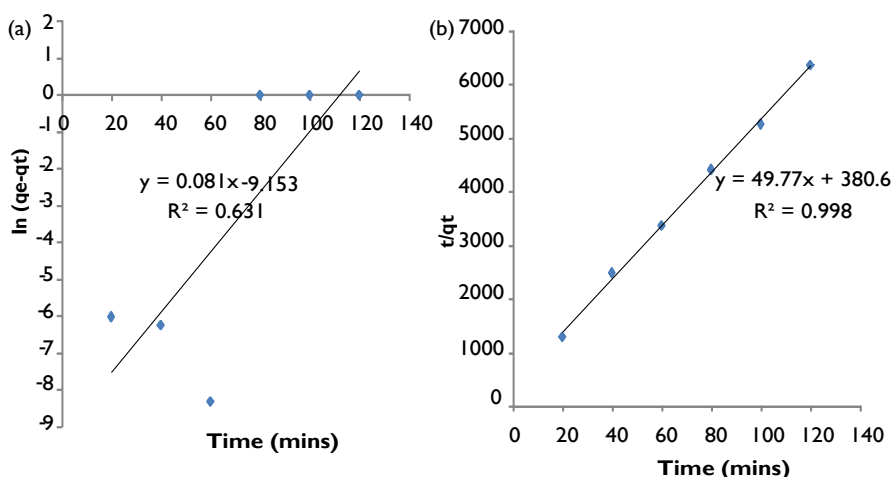


Fig. 3. Adsorption Kinetics of Lemon Peel Powder as (a) Pseudo-first-order (b) Pseudo-second-order Isotherms for Fluoride Adsorption. Test conditions: Adsorbent (2.5 g/L), Reaction time (100 min) and Fluoride solution (50ml)

Adsorption Kinetics Studies: The adsorption kinetics model explains the reaction processes whether a pseudo-first order reaction takes place in which diffusion occurs through a boundary or a pseudo-second model is involved where adsorption process is followed by chemisorption at the rate-control stage (Akafu *et al.*, 2019). The adsorption model with the best fit explains the adsorption experimental data better. The linear equation obtained from the pseudo-first order model (Figure 3a) is $y = 0.081x - 9.153$. While on the order hand, the linear equation obtained from the pseudo-second order plot is $y = 49.77x +$

380.6 (Figure 3b). The gradient and y-intercept obtained from the linear equation is used to calculate k_1 or k_2 , $q_{e, \text{cal}}$ respectively. The adsorption kinetics model parameter of fluoride adsorbed on lemon peel powder is shown in Table 2. The Pseudo second-order model fits better for the fluoride adsorption according to the relatively higher correlation coefficient ($R^2 = 0.998$) compared with the pseudo-first-order model ($R^2 = 0.631$). The adsorption amount of pseudo-second order model ($q_{e, \text{cal}} = 0.020 \text{ mg/g}$) agree well with the experimental values ($q_{e, \text{expt}} = 0.018 \text{ mg/g}$) compared to the calculated adsorption amounts of pseudo first-

order model ($q_{e,cal} = 1.06 \times 10^{-4}$ mg/g) which was not close to the value of experimental adsorption capacity. Hence, the adsorption of fluoride on lemon peel powder can be described well with pseudo second-order model in which the adsorption is based on the assumption that rate-determining step may be chemisorptions involving sharing or exchange of electrons between the ions and the adsorbent. This study is consistent with the findings reported previously by Tan *et al.* (2020). Since the fluoride adsorption is well described by the pseudo-second model, it can be assumed that the adsorption process occurs through a chemisorptions mechanism. It is likely that intra-particle diffusion may have occurred considering the boundary layer thickness of the adsorbent. It is interesting to note that an increase in the rate of a reaction with temperature may be associated with the availability of the active sites on the adsorbent by the increasing energy required for effective molecular collision. Hence, there is need to study the effect of temperature on adsorption that may be used in determining whether a reaction is exothermic or endothermic.

Conclusion: Activated carbon from lemon peel in this study exhibited excellent performance in the adsorption of fluoride in aqueous system, with a maximum removal efficiency of 94.90%. Based on findings of this study, it was recommended that further studies on regeneration of the adsorbent could be investigated to evaluate the efficiency of the activated carbon in terms of its reuse for a number of adsorption cycles.

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