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Eggshell modified with alum as low-cost sorbent for the removal of fluoride from aquatic environments: isotherm and kinetic studies

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ABSTRACT

The present study was conducted to investigate the performance of eggshells modified with alum for fluoride removal from aquatic solution and determine the isotherm and kinetic isotherms. This study was conducted on the batch mode and some effective parameters on the adsorption rate such as contact time, pH, adsorbent dose and adsorbate concentration were evaluated. The characteristic of the modified adsorbent was determined via X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results of XRD showed the peaks for modified eggshell powder with alum, which illustrated the presence of the alumina on the adsorbent. SEM images disclosed that the particles in the raw eggshells are broken down into small pieces with sharp-sided. In addition, the batch experiments showed that the residual concentration of fluoride has decreased as time increases. Also, the removal efficiency has decreased as pH increases toward alkaline phase. It is observed that increase in the adsorbent dosage subsequently decreases the residual concentration level of fluoride. The results of the experimental data showed that Dubinin–Radushkevich isotherm and pseudo-second-order model (high R^2) gave much better fit with data. According to the results, eggshell adsorbent modified with alum has been recommended for fluoride removal from aqueous solution.

Keywords: Adsorption; Eggshell; Alum; Fluoride removal; Isotherm and kinetic

1. Introduction

The entrance of wastewater with high fluoride concentration such as coal-fired power plant and aluminum smelters, as well as contact with mineral sediments, could lead to an increase in the fluoride amount in the water bodies. It is disclosed that low and high amounts of fluoride could create some adverse health effect on the human tissues. Skeletal and dental damages, fluorosis as well as DNA changes are the main disorders that could happen at high concentration of fluoride [1,2].

Fluoride, an imperative element for the body, should be provided from different resources including groundwater and drinking water, but beyond the level of 1.50 mg/L, was recommended by World Health Organization [3–5], it causes various health problems such as osteoporosis and even cancer [2,6–9]. There is a direct relationship between temperature and water consumption so that people in the climatically hot regions need more water and accordingly intake of fluoride from water becomes high [10,11]. Furthermore, the incorporation of a new technology to remove or reduce the fluoride concentration to the recommended level is required in these regions [7]. Recently, various technologies and methods have been widely developed toward these aims including precipitation [12], adsorption [4,13,14], membrane [5] and ion exchange [15,16]. High efficiency, simplicity of operation

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and low operational cost encourage the use of adsorption as a mass transfer process in water and wastewater treatment. Activated carbon is the most conventional adsorbent used in water and wastewater treatment plant, but high operating costs and problems related to its regeneration cause it to be less attractive for application in large scale. Natural and cheap adsorbent such as waste materials from agricultural that no need pretreatment could obtain more interest for removal of pollutants from aqueous solution [17–20]. Eggshell, which is low cost, waste material and abundant, is suggested to be used as an adsorbent in the water treatment process to remove fluoride [3]. The eggshell is full of calcium and modification of it with a trivalent element such as Al^{3+} and Fe^{3+} and alum could create a suitable substituent to remove fluoride from the aquatic solution since fluoride element has high affinity to trivalent elements [21]. Therefore, the present work was developed to examine the performance of eggshells modified with alum in fluoride removal from aquatic solution and investigate the equilibrium and kinetic isotherms fitted to experimental data.

2. Experimental setup

2.1. Materials

All the chemical reagents used in the present work including $Al_2(SO_4)_3$, NaF, KNO_3, KOH and fluoride were provided by Merck Company, Germany. Eggshell samples were collected from a grocery store in Tehran, Iran. To prepare the adsorbent, first eggshell samples were rinsed several times with deionized water to remove the impurity and pollutants. Then, samples were dried in an oven (MEMMERT, Germany) at 110°C for about 12 h. The dried eggshells were ground and screened through a set of sieves to 125 μm (mesh 120) and soaked in $Al_2(SO_4)_3$ solution (0.6 M) for 4 h. The resulting product was washed with distilled water and then dried in an oven at 103°C. The stock solution was prepared by dissolving 0.221 g NaF in 1 L of distilled water to give a concentration of 100 mg/L solution of fluoride and the required concentration of fluoride solution was prepared by serial dilution of 100 mg/L fluoride stock solution. Scanning electron microscopy (SEM) analysis was carried out to study the surface morphology of prepared modified eggshell powder. In order to detect the remaining fluoride concentration level, 10 mL of the filtrated sample was put into the cell of the spectrophotometer and then 2 mL of SPADNS reagent was added to the cell and shook for 2 min. Finally, the remaining fluoride concentration level was specified by spectrophotometer (HACH DR5000, USA) at the wavelength of 580 nm.

2.2. Batch adsorption of fluoride

Adsorption studies were performed in a fixed amount of eggshell powder and various pH (3–11), except the experiments of dosage effect, in a 250 mL glass Erlenmeyer flask as a reaction vessel. The experiments were performed at room temperature (about 25°C). The pH of the solution was adjusted to the desired level by adding a few drops of 0.1 M NaOH or HCl solution into the flask, when necessary. Different concentration levels of fluoride (3, 5, 7 and 9 mg/L) were placed in the capped volumetric flask and agitated during the equilibrium time and the effects of initial level concentrations of fluoride were analyzed in an accurate dosage of adsorbent derived from eggshells. To determine the equilibrium time of fluoride adsorption onto adsorbent, an accurate amount of adsorbent (0.25 g) was added to an Erlenmeyer flask containing 100 mL of fluoride solution. Afterward, the samples were taken every 20 min (20, 40, 60, 80 and 100 min). After the completion of the time periods mentioned previously, the samples were filtered and the remaining concentration levels of fluoride were detected with DR-5000 (HACH, USA). The equilibrium time was found to be 60 min. Each run of the experiment was triplicated and the value on average was reported. The amount of fluoride amount adsorbed on the adsorbent surface was calculated as follows [22,23]:

$$q = \left(C_0 - C_e\right) V / m \tag{1}$$

where q is the amount of fluoride adsorbed onto adsorbent (mg/g); C_0 and C_e (mg/L) are the concentration of fluoride at initial and equilibrium levels, respectively; V is the volume of solution (L) and m is the mass of the adsorbent (g).

Eq. (2) was used to calculate the removal the efficiency [24,25] as follows:

$$\text{Removal efficiency } (\%) = \frac{100\left(C_0 - C_e\right)}{C_0} \tag{2}$$

It should be mentioned that the most conventional isotherm and the kinetic model was evaluated for determining the effective variables on design and modeling of the fluoride adsorption at full scale.

3. Results and discussion

3.1. Characterization of the waste eggshell

Scanning electron microscope (FESESM, Hitachi, model: S4160) was employed to determine the surface morphology of modified eggshell powder derived from eggshell in raw state and activation stage. As can be observed from Figs. 1(a) and (b), the particles in the raw eggshells are broken down into small pieces with sharp-ends and agglomerated and formed a material which is suitable for adsorption process. There are as much enough as surfaces to adsorb the fluoride as a contamination.

XRD analysis was applied for mineral identification and to characterize the raw eggshell and modified eggshell powder with X-ray diffractometer (XRD; model: XD-5A; Japan) using Cu Kα (λ = 1.541 Å).

As viewing Fig. 2, the graph related to raw adsorbent has many peaks, which main ones fluctuate around 2θ = 23.32°, 29.68°, 31.04°, 35.88°, 40.56°, 42.20°. These peaks are evidenced to be attributed to $CaCO_3$. However, the peaks observed for modified eggshell powder with alum in 2θ = 14.68°, 20.68°, 25.60°, 29.04°, 31.84°, 33.36° emphasize the presence of alumina on the adsorbent. Therefore, these peaks indicate that the modification of eggshell powder was made in a proper way [24].

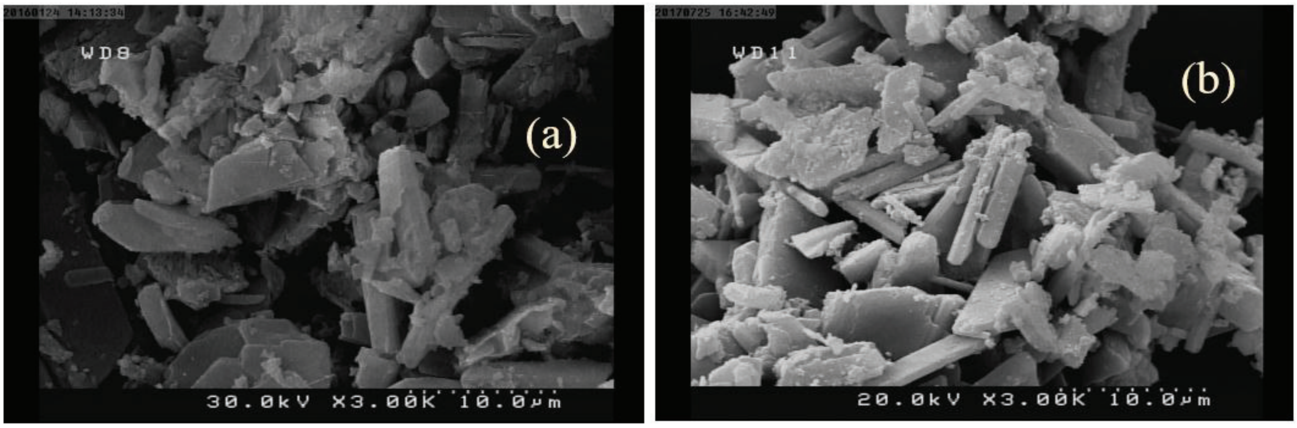

Fig. 1. SEM micrograph: (a) raw eggshell and (b) modified eggshell.

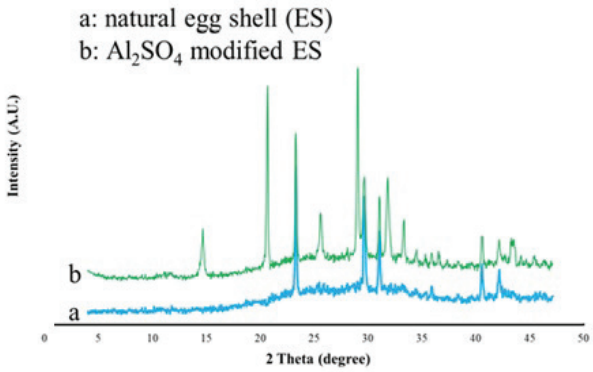

Fig. 2. XRD of eggshell and modified eggshell with alum for adsorption of fluoride.

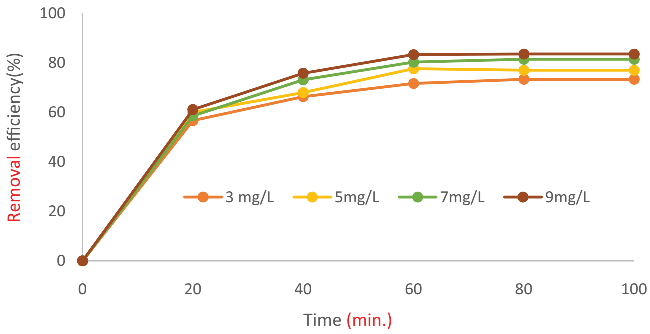

Fig. 3. Effect of contact time on the adsorption of fluoride onto modified eggshell at various amount of fluoride (pH: 6, adsorbent dose: 0.25 g/100 mL).

3.2. Effect of contact time

Adsorption experiments were carried out as a function of time in range 0–100 min with interval of 20 min, considering other experimental condition, including pH 6, agitation rate 200 rpm, adsorbent dosage 0.25 g/100 mL for four different concentration levels of fluoride 3, 5, 7 and 9 mg/L. As viewing Fig. 3, as time proceeds, the residual concentration of fluoride has decreased; on the other hand, the removal efficiency increased. In addition, the significant removal of the adsorbate took place at initial reaction time (initial 20 min). The rapid adsorption rate of fluoride might be associated with the high affinity of fluoride to the active adsorption sites on the modified eggshell. The decrease in residual fluoride concentration meant increase in the amount adsorbed as a function of time until the adsorption of fluoride approached to remain constant, implying that adsorption equilibrium has been reached. After a time period of approximately 60 min, a gradual decline for limiting adsorption capacity was observed; therefore, in the present work time equal to 60 min with maximum adsorption (83.3%) was considered as optimum contact time which fluoride is in contact with modified powdered eggshell as an adsorbent. After 60 min, the fluoride adsorption rate on an eggshell powder is found to decline due to the decrease of suitable sites for adsorption [3].

3.3. Effect of pH

The effect of pH on fluoride removal was examined in the range 3–11 for four different concentration levels of fluoride, considering other parameters constant influencing in the process including, agitation rate: 200 rpm, contact time: 60 min and adsorbent dosage: 0.25 g/100 mL. Fig. 4 indicates the effect of pH as an important factor influencing the adsorption process on fluoride removal. As can be observed from Fig. 4, the removal efficiency has decreased as pH increases toward alkaline phase, which tends to decrease the affinity for fluoride. The highest removal efficiencies for different concentrations were observed about 3, so that, determined as optimum pH. In addition, the dominance of hydroxyl ions at high pH can compete with fluoride ions to occupy the active site on the adsorbent surface. Therefore, the acidic pH could create a good condition for adsorbing the fluoride ions.

The pHzpc for modified eggshell powder with alum was 6.4. Thus, the surface of modified eggshell powder will be positively charged at pH < 6.4, and the electrostatic interactions between fluoride ions and the adsorbent enhanced.

3.4. Effect of initial fluoride concentration and adsorbent dosage

The effect of varying adsorbent dosage of powdered activated eggshell on fluoride removal efficiency was performed in different dose usage including 0.15, 0.25, 0.5, 0.75, 1, 1.5, 2 g/100 mL for four different concentration levels of fluoride including 3, 5, 7 and 9 mg/L, considering pH: 6, agitation rate: 200 rpm and contact time: 60 min. As can be seen from Fig. 5, it is obviously observed that increase in the adsorbent dosage up to 1 g/100 mL subsequently decreases the residual concentration level of fluoride and on the other hand increases the removal efficiency. Adsorbent dosage with high amount typically provide large surface spaces for adsorption process, but it should be noted that high amount of adsorbent is not acceptable in the viewpoint of economics [26]. Therefore, in the present research adsorbent dosage equal to 0.25 g/100 mL with maximum adsorption (82.5%) was selected as the optimum dosage. This amount of reduction is enough to create an acceptable source of potable water to the standard limit. Also, enhancement of fluoride removal with increasing adsorbent amount could be associated with the increase in the free available active adsorption sites. On the other hand, the high removal efficiency of fluoride carried out at low concentrations of fluoride. This might be due to sufficient free available adsorption active sites at low concentration of fluoride.

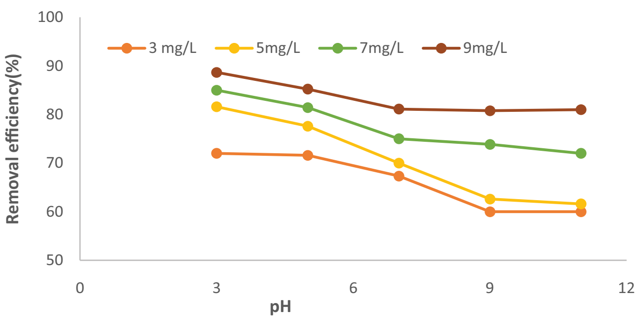

Fig. 4. Effect of pH on the adsorption of fluoride at various pH (contact time: 60 min; adsorbent dose: 0.25 g/100 mL).

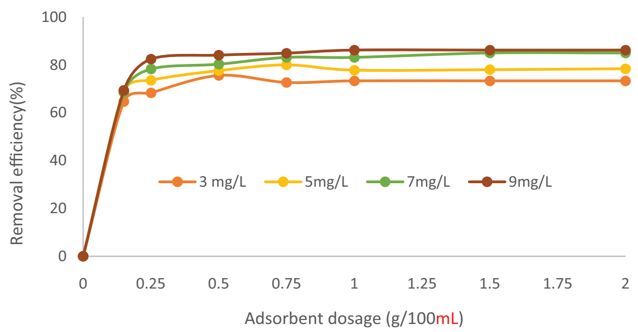

Fig. 5. Effect of adsorbent dose and initial fluoride concentration on the fluoride adsorption (contact time: 60 min; pH: 6).

3.5. Adsorption isotherms

Equilibrium modeling is a major part of a sorption study and has a great influence on the economy of the process [27,28]. As presented in Table 1, in the present study, the data points in equilibrium models give a much better fit to the Dubinin–Radushkevich (D–R) isotherm. Contrary to Langmuir and Freundlich models, the D–R isotherm does not assume a homogeneous surface or constant sorption potential with definite adsorption sites where have same adsorption energy or even two-dimensional adsorbate layer on the surface. The D–R model considers that the adsorption occurs in multiple layer and involves Van der Waals forces. The D–R isotherm also is temperature and concentration dependence. The plot of various models of adsorption isotherm is shown in Fig. 6. Based on the D–R model, the maximum adsorption capacity (q_{max}) for fluoride removal onto eggshell was 6.11 mg/g which illustrates the adsorption capacity of eggshell was enough and can compete with other adsorbents that were found by studies using the raw or modified pumice [29], modified Lemna minor [30], modified *Azolla filiculoides* [14], sorghum and canola [31].

3.6. Kinetic study

Data related to the kinetic studies are vital for disclosing the reaction dynamics of adsorption. In addition, optimal conditions of the batch mode in the full scale could be determined through kinetic studies. Design and modeling of the adsorption process and the prediction of the rate of

Table 1
Linear forms and results obtained from isotherm studied of fluoride adsorption onto the modified eggshell

Isotherm	Formula	Plot	Parameter		Reference
Langmuir	$q_e = \frac{q_m b C_e}{1+bC_e}$	$\frac{C_e}{q_e}$ vs. C_e	q_{max} (mg/g)	–0.361156564	[32]
			K_L (L/mg)	–0.560691189	
			R^2	0.880	
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e$ vs. $\log C_e$	K_F (mg/g(L/mg)$^{1/n}$)	0.194348021	[33]
			N	0.402829758	
			R^2	0.963	
Temkin	$q_e = \frac{RT}{b}\ln(k_T C_e)$	q_e vs. $\ln C_e$	k_t (L/mg)	0.777610697	[34]
			B_1	1.405448918	
			R^2	0.919	
Dubinin–Radushkevich	$q_e = q_m \exp(-\beta\varepsilon^2)$	q_e vs. ε^2	q_{max} (mg/g)	6.11002E-07	[35]
			β	3.103648384	
			R^2	0.968	

adsorption could be carried out according to the kinetic study [36]. Thus, pseudo-first and pseudo-second-order, Elovich and intraparticle diffusion kinetics have been determined in the present study. The physio-chemical properties of the adsorbent, adsorbate and experimental system could affect the kinetics of adsorption. In addition, the rate of sorption reaction has been estimated through the kinetic adsorption study which is required for choosing the optimum operating conditions at full scale. The pseudo-second-order coefficients (q_e and k_2) show the adsorption rate which is used for the design of the full-scale process. The results obtained were confirmed with previous studies [18,37]. The linear equations and results obtained from the kinetic studies are shown in Table 2. Pseudo-second-order model was best fitted with the results of kinetic experiments rather than other models. The R^2 values of this model were in the range of 0.97 to 0.99. In addition, the plot of kinetic models evaluated in this study is presented in Fig. 7.

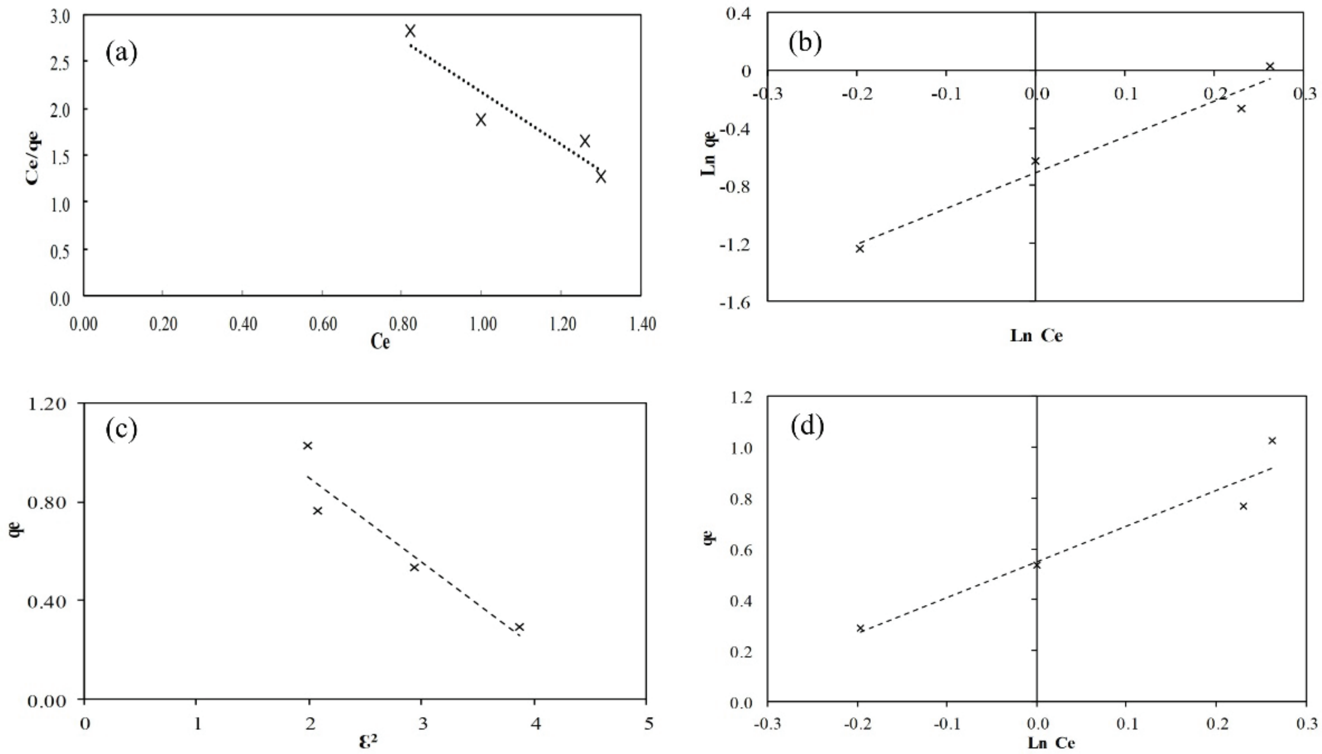

Fig. 6. Plots of isotherm models studied for fluoride adsorption onto modified eggshell: (a) Langmuir, (b) Freundlich, (c) Dubinin–Radushkevich and (d) Temkin.

Table 2
Results of kinetic model studies related to the fluoride adsorption onto the modified eggshell

Kinetic	Linear equation	Plot	Constant	Value		
				3 mg/L	5 mg/L	7 mg/L
Pseudo-first-order	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$	$\log(q_e - q_t)$ vs. t	k_1	0.025	0.029	0.032
			q_e (calc)	0.981	0.907	0.653
			R^2	0.933	0.969	0.968
Pseudo-second-order	$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t$	$\frac{t}{q_t}$ vs. t	k_2	0.050	0.036	0.025
			q_e (calc)	0.997	0.865	0.839
			R^2	0.971	0.998	0.997
Elovich	$q_e = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t$	q_e vs. $\ln t$	α	0.039	0.062	0.258
			β	4.496	5.444	7.435
			R^2	0.935	0.966	0.929
Intraparticle diffusion	$q_t = K_{dif} t^{0.5} + C$	q_t vs. $t^{0.5}$	K_{dif}	0.050	0.040	0.029
			C	0.114	0.232	0.404
			R^2	0.943	0.902	0.865

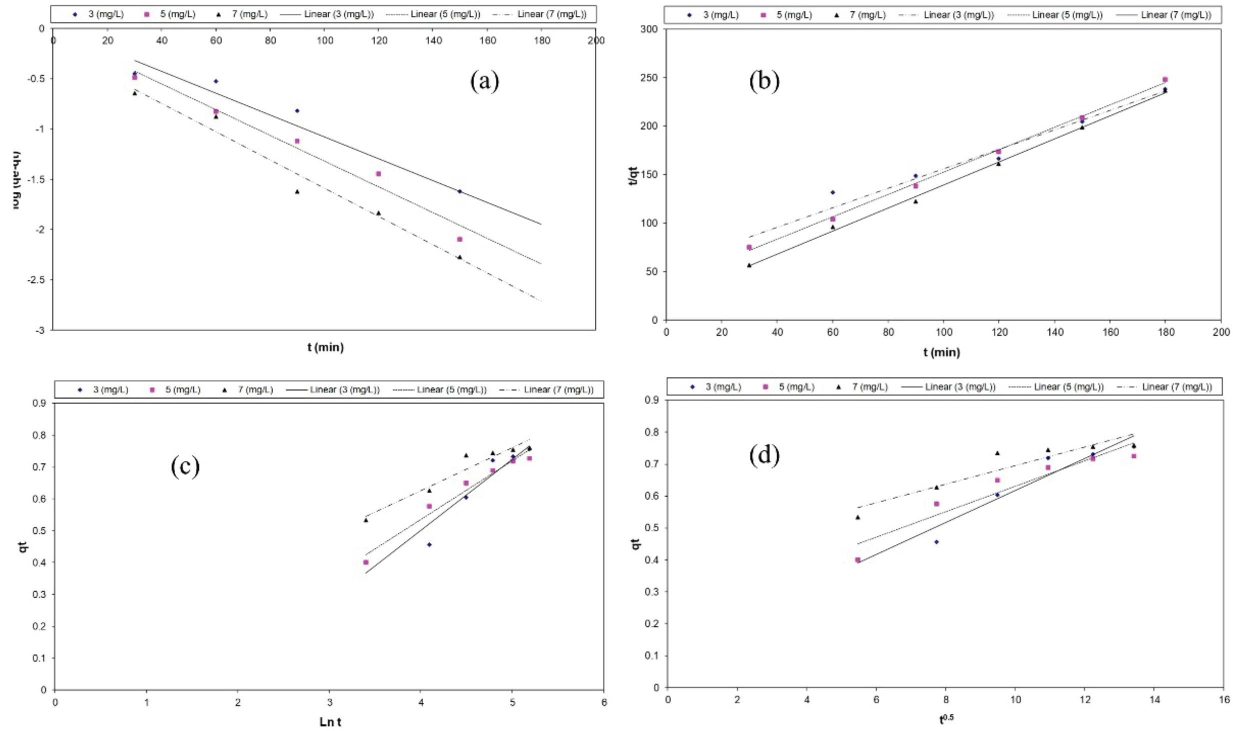

Fig. 7. Plots of kinetic models studied for fluoride adsorption onto modified eggshell: (a) pseudo-first-order, (b) pseudo-second-order, (c) Elovich and (d) intraparticle diffusion.

4. Conclusion

Herein, eggshell modified with $Al_2(SO_4)_3$ was used for adsorption of fluoride from aqueous solution. Generally, XRD showed the peaks for modified eggshell powder with alum which illustrated the presence of the alumina on the adsorbent. SEM images presented that the particles in the raw eggshells are broken down into small pieces with sharp-sided and formed a material for adsorption of fluoride. In addition, the batch experiments showed that the residual concentration of fluoride has decreased as time proceeds and the significant removal of the adsorbate took place at initial time reaction (initial 20 min). Also, the highest removal efficiency was obtained at pH: 3. It is obviously observed that increase in the adsorbent dosage subsequently decreases the residual concentration level of fluoride. The results showed that adsorbent dosage equal to 0.25 g/100 mL with maximum adsorption 82.5% was selected as optimum dosage. The experimental data pointed that the results of the fluoride adsorption onto modified eggshell with alum gave a much better fit to the Dubinin–Radushkevich (D–R) isotherm (R^2: 0.96) and pseudo-second-order model (R^2: 0.97 to 0.99). Based on the D–R model, the maximum adsorption capacity (q_{max}) for fluoride removal onto eggshell was 6.11 mg/g.

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