

# Kinetics of Fluoride Adsorption on Mixed Oxide Nanocomposites: Analysis

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**Abstract:** The prevalence of high fluoride concentration in water is a global problem. High fluoride concentration is a health hazard which results in dental and skeletal fluorosis. In an effort to reduce the detrimental effects of fluoride a number of technologies are in use but adsorption has proved to be the most effective and economic fluoride removal technology. The advent of nanotechnology introduced nanoadsorbents as an alternative to bulk adsorbents. Nanocomposites are an important class of adsorbents that have gained wide interest from researchers. Sorption kinetics is one of the most important parameters that are used in evaluation of the efficiency of an adsorbent. There are various mathematical models in use but in this paper attention is paid to adsorption reaction models which are mainly used by researchers to fit kinetic data for nanoadsorbents.

**Index Terms:** adsorption; Fluoride; reaction models; nanocomposites; kinetic models

## 1 INTRODUCTION

The dissolution of fluoride rich rocks and industrial waste streams with high fluoride concentration are the main source of high fluoride concentration in drinking water [1]. Drinking water with high fluoride concentration may cause dental and skeletal fluorosis and according to World Health Organization (WHO) the maximum acceptable concentration is below 1.5mg/L [2]. Fluorosis has been described as an endemic disease of the tropical climate but high fluoride waters occur in many geographical regions. Endemic of fluorosis is found in Argentina, U.S.A., Morocco, Algeria, Libya, Egypt, Jordan, Turkey, Iran, Iraq, Kenya, Tanzania, S. Africa, China, Australia, New Zealand, Japan, Thailand, Canada, Saudi Arabia, Persian Gulf, Sri Lanka, Syria, India, etc [3, 4]. In many cases communities living in areas with high fluoride in drinking water have no alternative source of health clean water. Hence their water has to be treated if it's to be safe for drinking. There are many reported methods for reducing fluoride concentration in water and these are adsorption, ion exchange, precipitation, electro-dialysis and reverse osmosis [5]. Adsorption has been found to be one of the most effective, economic and environmentally friendly as compared to the other techniques [6]. There are many adsorbents that are available in literature such as bone char, activated alumina, amorphous alumina, activated carbon, red mud and some low cost adsorbent [7]. The emergence of nanotechnology has introduced nanoadsorbents which are unique and have excellent physical and chemical properties which aid adsorption process. The nanoadsorbents have small size and high to surface ratio which results in high adsorption capacity and fast kinetics as active adsorption sites are on the surface [8]. The objective of this work is to provide a detailed analysis of fluoride sorption on nanocomposite. This is because nanocomposites have shown good results in reducing

fluoride to below the recommended limit hence they are going to be an important part of fluoride removal technology. Adsorption kinetics is very important for designing of continuous flow system and a detailed understanding will result in excellent adsorption equipment design. The mathematical models will be discussed and the various manipulations that are done to linearly fit the data to the models. A brief analysis of application of these models to nanocomposites is also included.

## 2 KINETIC MODELS

The kinetics of adsorption is significant in the evaluation of the performance of a given adsorbent and it provides insight into the reaction pathways and the mechanism of reaction. In general adsorption kinetics is the basis that is used to determine the performance of any flow-through system [9]. A number of mathematical models have been proposed to describe adsorption data and it is mainly divided into adsorption reaction model and diffusion models. Adsorption diffusion models are based on three steps which are liquid film diffusion, diffusion in the liquid which is internal diffusion and adsorption of adsorbate on active sites. The reaction models are based on chemical reaction kinetics where the whole process is considered not individual process [10]. Adsorption reaction models are the ones that apply to adsorption of nanoadsorbent as the active adsorption sites are found on the surface.

## 3 ADSORPTION REACTION MODELS

There are a number of reaction models in use and the models which are discussed here have been applied mainly to nanoadsorbents. Nanoadsorbents have their active adsorption sites on the surface hence they are characterized by fast sorption kinetics as pore diffusion length is very small or reduced. The models discussed in this paper are

pseudo-first-order, pseudo-second-order and Elovich's equation.

### 3.1 Pseudo-first-order model

Lagergren (1898) proposed a model that is based on kinetics of liquid-solid phase adsorption [10]. The pseudo-first-order equation is represented as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

Where  $q_e$  and  $q_t$  (mg/g) are the adsorption capacities at equilibrium and time  $t$  (min), respectively.  $k_1$  is the pseudo-first-order rate constant for the kinetic model. Integrating Eq. (1) with the boundary conditions of  $q_t = 0$  at  $t=0$  and  $q_t = q_t$  at  $t=t$ , and rearranging yields:

$$\log(q_e - q_t) = \log q_e - \frac{tk_1}{2.303} \quad (2)$$

The plot of  $\log(q_e - q_t)$  versus  $t$  should give a straight line from which  $k_1$  and  $q_e$  can be calculated from the slope and intercept respectively.

### 3.2 Pseudo-second-order model

The model was developed by Ho and Mckay in 1998 to describe the adsorption of some metal ion onto adsorbent [7]. The driving force is proportional to available fraction of active sites. The rate expression is given as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

Where  $q_e$  and  $q_t$  (mg/g) are the adsorption capacities at equilibrium and time  $t$  (min), respectively.  $k_2$  is the pseudo-second-order rate constant (given in units of  $g\ mg^{-1}\ time^{-1}$ ). Integrating Eq. (3) with the boundary conditions of  $q_t = 0$  at  $t=0$  and  $q_t = q_t$  at  $t=t$ , and rearranging yields:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + k_2t \quad (4)$$

The plot of  $\frac{t}{q_t}$  versus  $t$  provides the value of  $k_2$  and  $q_e$  from the intercept and straight line. The initial adsorption rate can be obtained as  $\frac{q_t}{t}$  when  $t$  approaches zero: This equation has been successfully applied to the adsorption of metal ions, dyes, herbicides, oils, and organic substances from aqueous solutions [11]

### 3.3 Elovich's equation

This model is based on chemisorption phenomena and is expressed as

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (5)$$

nanocomposites.

Where  $q$  represents the amount of gas adsorbed at time  $t$ ,  $\beta$  is adsorption rate and  $\alpha$  is the initial adsorption rate. The linear form of equation 5 is

$$q = \left(\frac{2.3}{\alpha}\right) \log(t + t_0) - \left(\frac{2.3}{\alpha}\right) \log t_0 \quad (6)$$

The plot of  $q$  versus  $\log(t + t_0)$  yield a straight line if the data is a good fit this model is applied for chemisorption of gases on heterogeneous solids [10].

## 4 NANOCOMPOSITES

A number of nanocomposite adsorbents have been used for fluoride removal in literature and their data have been fit to the various kinetic models and it has been seen that most of the data fit well to pseudo-second-order kinetics. Xiaoli et al. [12] found that adsorption of fluoride on  $Fe_3O_4@Al(OH)_3$  fit well with pseudo-second-order kinetics. The smaller size of nanoadsorbents results in fast kinetics which gave an equilibrium time of 60 minutes. Sorption kinetic studies done by S.K. Swain et al [13] showed that the data had a correlation coefficient of 0.997 for pseudo-second-order kinetic. They also found that the value for the calculated adsorption capacity was close to the experimental adsorption capacity. The data also gave a good fit to the intraparticle diffusion and it was found that pore diffusion may not be the only rate controlling step. N. Minju et al [14] analyzed kinetic data using pseudo-first order and pseudo-second-order kinetic models. The kinetic data was well predicted by pseudo-second-order model. The rapid uptake of fluoride was attributed to the reduction in distance an adsorbate travels to reach active sites hence diffusion resistance is reduced resulting in fast kinetics.

Time dependent adsorption studies for  $CeO_2-ZrO_2$  were performed at different temperatures and analyzed using pseudo-second-order kinetics. Fluoride adsorption was found to increase with an increase in temperature. Pseudo-second-order kinetic model gave the best fit for the nanocages and also there was rapid fluoride uptake in the first 10 minutes with equilibrium being reached after 24 hours [15]. Pseudo-first order and pseudo second-order rate equations were used to model fluoride adsorption kinetics for Mg-doped nanoferrhydrite. The pseudo second-order model fitted well with  $r^2$  values of 0.98 and the calculated  $q_e$  values estimated from the pseudo-second-order models matched very well with experimental [16]. The kinetic models that fit well to the kinetic data are presented in table 1. It can be seen that pseudo-second-order kinetic model is mostly applicable to the kinetics of

Table 1: Kinetic models for nanocomposites

Nanocomposite	Best fit kinetic model	Reference
Fe <sub>3</sub> O <sub>4</sub> @Al(OH) <sub>3</sub>	pseudo-second-order	(12)
Fe(III)-Zr(IV) binary mixed oxide	pseudo-second-order	(13)
Magesium oxide -coated magnetite (Fe <sub>3</sub> O <sub>4</sub> )	pseudo-second-order	(14)
CeO <sub>2</sub> -ZrO <sub>2</sub>	pseudo-second-order	(15)
Mg-doped nanoferrihydrate	pseudo-second-order	(16)

## 5 CONCLUSION

Adsorption reaction models are mainly applied to fit kinetic data for nanoadsorbents. The two most commonly used reaction models are pseudo-second-order and pseudo-first-order. Pseudo-second-order has been found to fit best to the kinetic data of fluoride adsorption on nanocomposites. This indicates that kinetics of fluoride adsorption on nanocomposites has chemisorption as one of

the factors that is controlling the sorption kinetics. Sorption studies are still important because of their significance in adsorption evaluation and application.

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