FLUORIDE REMOVAL FROM AQUEOUS SOLUTIONS BY ZINC OXIDE NANOPARTICLES

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ABSTRACT: High concentrations of fluoride ion (F) above the optimum level can lead to dental, skeletal, and non-skeletal fluorosis. The data presents a method for F removal from F-containing wastewaters. Zinc oxide nanoparticles (ZnO NPs) were applied as an adsorbent to remove F ions from aqueous solutions. The structural properties of the ZnO NPs were analyzed using scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) techniques. A batch adsorption experiment was conducted to consider the influence of different parameters such as pH (2–10), contact time (20–100 min), initial F concentration (15–40 mg/L), and ZnO NPs dosage (0.02–0.09 g/L). Adsorption kinetic and isotherm data were also calculated. Optimum conditions of pH 6, adsorbent dose: 0.09 g/L, time: 60 min, and initial F concentration: 20 mg/L were obtained at 97.5% efficiency. The kinetic data followed the Ho kinetic model with correlation coefficient (R^2) of 0.999 at 20 mg/L. The isotherm data fitted into the Langmuir isotherm. The experimental data obtained indicated that the use of ZnO NPs adsorbent for the reduction of F in F containing wastewater is feasible.

Key words: Aqueous solution; Fluoride; Isotherm; Kinetic; Zinc oxide nanoparticles.

INTRODUCTION

The mineral compounds present in aqueous natural resources or water contaminating sources play a significant role in the public health. Fluoride (F), the ion of the element fluorine, is a mineral that adversely affects water quality, and is found in many surface and groundwater resources.[1,2] The concentration of F in these waters ranges between 10 and 1,000 mg/L.[3] Its allowable limit in drinking water, according to the WHO standard, is 1.5 mg/L, although lower Country Standards have also been set such as 1 mg/L in India and 0.6 mg/L in Senegal, West Africa.[4] A rider to the Indian limit is that the "lesser the fluoride the better, as fluoride is injurious to health." Fluorine compounds are found in industrial applications and they are used widely in the production of semiconductors, fertilizers, high purity graphite, and aluminum.[5,6] Over 20 developed and developing countries have regions with endemic fluorosis. These countries include Argentina, USA, Morocco, Libya, Algeria, Japan, Iraq, Egypt, Jordan, Kenya, Sri Lanka, China, Saudi Arabia, Thailand, India, Turkey, Syria, South Africa, Tanzania, and Iran.[7,8] Long term exposure to high levels of F leads to its accumulation and may result in toxicity with dental, skeletal, and non-skeletal fluorosis, including altered DNA structure, impaired muscle strength, digestive disorders, liver impairment, and endocrine disturbances such as disturbed thyroid hormone metabolism and reduced growth hormone.[9-15] In addition, it influences the metabolism of some elements such as

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calcium and potassium.[16] Effluents containing F must be properly treated before their discharge into water bodies.

Different methods such as ion exchange, reverse osmosis, electrodialysis, adsorption, electrocoagulation, and chemical treatment have been applied for F reduction.[17-22]

Many of these methods, such as electrochemical techniques and membrane processes, cannot be used on a large scale due to high operational costs, repair and maintenance costs, high electricity consumption, production of toxic by-products, and complex operation. Adsorption can be considered as an effective method for F removal.[4] The adsorption process, which is controlled by mainly physical forces such as Van der Waals forces, hydrogen bonds, polarity, and dipole-dipole interaction, is one of the most effective methods for the treatment of polluted waters.[3]

Adsorption by nanoparticles is an environmentally friendly technology, which has attracted a great deal of attention as an effective approach for removing contaminations.[23] Due to their unique properties and promising applications in water treatment and purification systems, nanometer-sized particles have been competently studied during the last few decades. The high efficiency of nanoparticles in adsorption, high specific surface area, high reactivity, numerous active sites, and ability of nanoparticles to be dispersed in aqueous solutions are among the main advantages of this method. The high surface to volume ratio of nanoparticles increases their adsorption capacities as adsorbents and gives a greater density of adsorption sites.[24-26] Zinc oxide nanoparticles (ZnO NPs) are a catalyst with high efficiency, because of their relatively greater surface area and the increased effect of their small quantum size.[27] The main purpose of this study is to investigate the efficiency of ZnO NPs in the adsorption of F from an aqueous solution. The adsorption isotherm and kinetic models were also applied in the study.

MATERIALS AND METHODS

Characterization of zinc oxide nanoparticles (ZnO NPs): The spectral properties of the adsorbent were determined by using Fourier transform infrared (FTIR) and scanning electron microscopy (SEM). SEM was done on the adsorbent to determine its surface morphology using a Mira 3-XMU instrument. The FTIR was done on a JASCO 640 plus machine (4000–400 cm^{-1}) to determine the functional groups present in the ZnO NPs taking part in the adsorptive removal of F.

Materials: Zinc oxide nanoparticles (ZnO NPs) were supplied by Sigma-Aldrich, USA. All reagents [sodium hydroxide, NaOH (98% purity) and hydrochloric acid, HCl (99% purity)] were of analytical grade and purchased from Merck (Germany). All the solutions were prepared using deionized water.

Adsorption experiments: The adsorption experiment was conducted with batch mode using the one-factor-at-a-time (OFAT) method, that is, keeping all but one factor constant and varying the other factor to get its optimum condition. In this research, the influence on the removal efficiency was examined for pH (2–10), contact time (20–100 min), initial F concentration (15–40 mg/L), and ZnO NPs dosage (0.02–0.09 g/L). A known mass of adsorbent was added to 1 L of water sample containing various concentrations of F. The pH of the water sample was adjusted by adding 0.1 N HCl or 0.1 N NaOH. The removal efficiency was

determined by varying the different parameters such as pH (2–10), contact time (20–100 min), F concentration (15–40 mg/L), and ZnO NPs dosage (0.02–0.09 g/L). To create optimal conditions, a shaker with 150 rpm was used. After each experimental run, the solution was filtered and the filtrate analyzed for the residual F concentration. The initial and residual F concentrations in the solutions were analyzed by a UV–Visible recording spectrophotometer (Shimadzu Model: CE-1021-UK) at a wavelength of absorbance (λ_{max}): 570 nm. [28]

Data analysis: Equations 1 and 2 were applied to calculate the F adsorption capacity and ZnO NPs adsorption efficiency, respectively.[29,30]

$$\text{Adsorption capacity } q_e \quad = \quad \frac{(C_0 - C_e)\, V}{M} \qquad \text{........................Equation 1}$$

$$\text{Adsorption efficiency \%} \quad = \quad \frac{(C_0 - C_e)\, V}{C_0} \times 100 \qquad \text{.................Equation 2}$$

Where:

q_e	=	adsorption capacity (mg/g)
C_0	=	initial fluoride concentration (mg/L)
C_e	=	equilibrium fluoride concentration (mg/L)
V	=	volume of fluoride solution (L)
M	=	weight of fluoride (g)

RESULTS AND DISCUSSION

Characterization of zinc oxide nanoparticles (ZnO NPs): The spectral properties of the adsorbent were determined by using FTIR and SEM (Figures 1A and 1B).
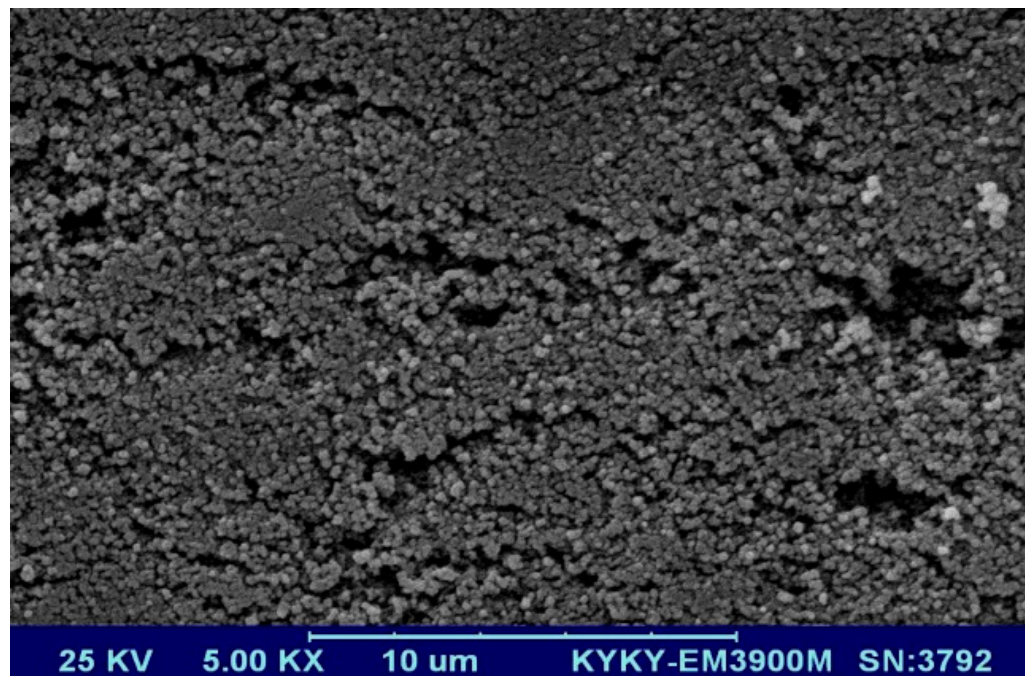

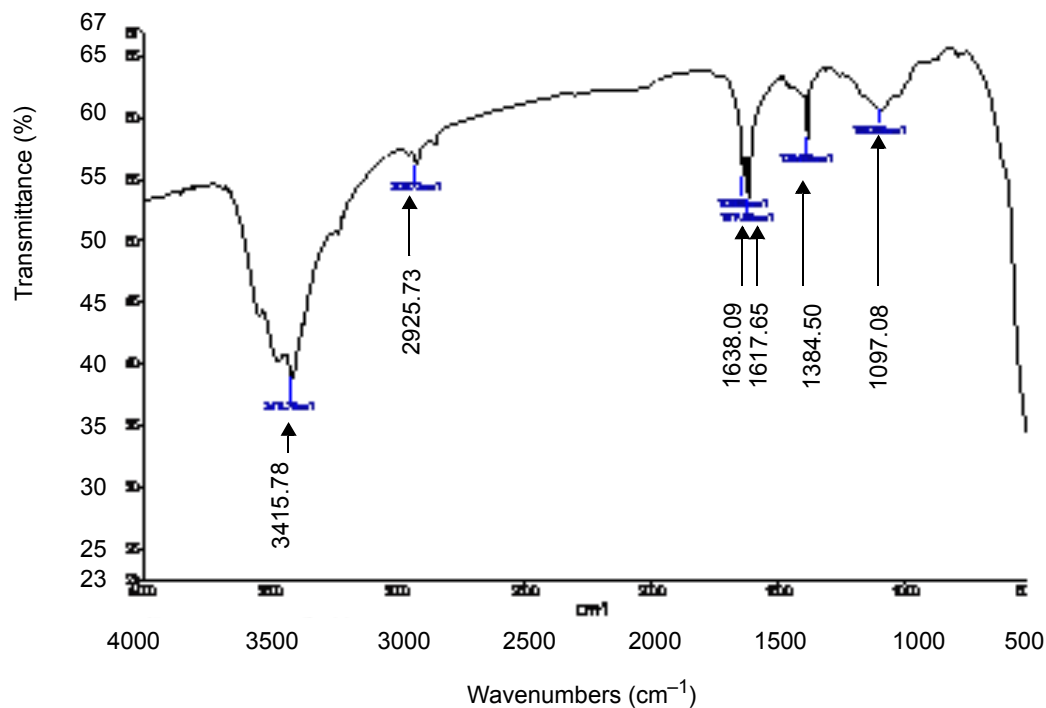**Figure 1A.** Scanning electron microscopy (SEM) image of ZnO NPs.

Figure 1B. Fourier transform infrared (FTIR) spectroscopy of ZnO NPs.

The functional groups existing in the ZnO NPs obtained from the FTIR analysis, which took part in the adsorption process are listed in Table 1. In the SEM image, the ZnO NPs consist of lamellar-like structures.

Table 1. Functional groups present in ZnO NPs

Wave number (cm^{-1})	Bond source	Functional group	Peak description
1097.08	C–O stretch	alcohols, carboxylic acids, esters, ethers	
1384.50	C–H rock	alkanes	
1617.65, 1638.09	C–C stretch (in–ring)	aromatics	
2925.73	C–H stretch	alkanes	strong, broad, and multi-banded
3415.78	O–H stretch, H–bonded	alcohols, phenols	strong and broad bands

Effect of initial pH: pH plays a significant role in controlling the surface charge of an adsorbent, the degree of ionization of the adsorbate in the solution, and dissociation of different functional groups on the active sites of the adsorbent.[30,31] Effect of different pH (2–10) on the adsorption of fluoride (F) onto ZnO NPs at contact time of 60 min, concentration of 15 mg/L, and adsorbent dosage of 0.09 g/L

are shown in Figure 2. Higher removal efficiency was obtained at pH 6 (Figure 2). The amount of F adsorbed also decreased from 1.15 mg/g to 0.28 mg/g at pH 2 to pH 6, respectively. F is an anion and the point of zero charge, pH_{ZPC} for ZnO NPs was found to be 7.5.[32] Thus, below 7.5, the surface of the ZnO NPs is positively charged and attracted anions from the dye solution. At pH higher than this value, the surface of ZnO NPs is negatively charged and attracted cations. At a low pH, the adsorbent surface possessed a positive charge[3] and the F in aqueous solution is negatively charged. The increase in the adsorption efficiency at low pH was due to an increase in the number of positively charged sites.
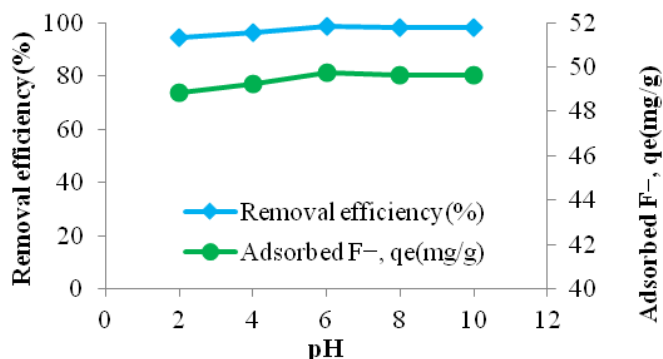

Figure 2. Effect of pH on the removal efficiency of fluoride (F) on ZnO NPs. Contact time= 60 min, dosage= 0.09 g/L, initial F concentration= 15 mg/L).

Effect of adsorbent dose: The effect of adsorbent dose on the removal of F was studied by varying the dose of adsorbent from 0.02 to 0.09 g/L. From Figure 3, it is evident that the adsorbent dose significantly influenced the amount of F adsorbed. When the adsorbent concentration was increased from 0.02 to 0.09 g/L at F concentration 15 mg/L, the efficiency increased from 73.75% to 97.5%. The biosorption capacity (q_e) on ZnO NPs also decreased from 7.375 to 2.22 mg/g when the ZnO NPs dosage was increased from 0.02 to 0.09 g/L. In fact, the level of deletion significantly depends on the number of active sites and by increasing the dosage of nanoparticles to an appropriate level, the number of available adsorption sites will increase as a result of increased adsorption capacity.[33] However, as the study shows, if the level of nanoparticles be higher than a particular extent, it will has no more effect on deletion and it even may result to the decrease of efficiency.[34]
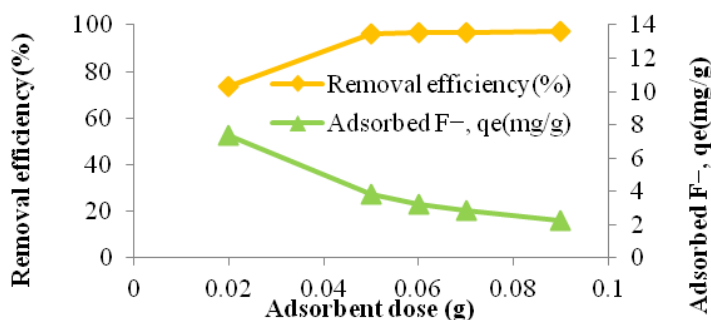

Figure 3. Effect of adsorbent dose on the removal efficiency of fluoride (F). (Contact time= 60 min, pH= 6, initial F concentration= 15 mg/L).

536 Research report
Fluoride 53(3 Pt 2):531-541
July-September 2020

Fluoride removal from aqueous solutions by zinc oxide nanoparticles
Mahvi, Rahdar, Igwegbe, Rahdar, Ahmadi

536

Effect of contact time and initial F concentration: The influence of initial F concentration on the removal of F by ZnO NPs was examined by changing the initial F concentration from 15 to 40 mg/L at pH 6 using F dosage of 0.06 g/L. Figure 4 shows that the removal efficiency declined with increasing F concentration from 20 to 40 mg/L at different times.
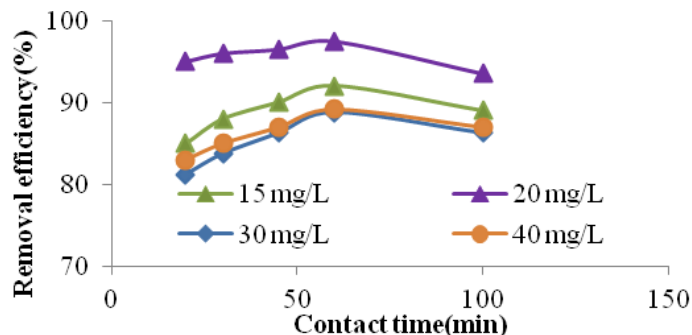

Figure 4. Effect of the contact time and the initial fluoride (F) concentration on the removal efficiency of F. (ZnO NPs dosage=0.06 g/L, pH =6).

Figure 4 shows the adsorption efficiency versus time at different F concentrations. The time of equilibrium was very short. The maximum removal efficiency of the different F concentrations was observed at the contact time of 60 min. The removal efficiency was higher at the early times. After this time, the slope of diagram slowed and at a specific time placed in equilibrium. The F adsorption in the initial minutes was high but after a while, the adsorption rate decreased because of reduced F concentration and reduction of the active sites present in adsorbent surface.[35] The active sites were available in the initial steps and after starting the reaction, they were all occupied with F molecules. Li et al. found the adsorption rate of fluoride on aligned carbon nanotubes was decreased after 60 minutes, at initial F concentrations of 15, 20, 30, and 40 mg/L, because of a decrease in the number of active sites.[36]

Adsorption isotherms: An important physiochemical subject in terms of the evaluation of sorption processes is the sorption equilibrium. In fact, the isotherm provides a relationship between the amount of F adsorbed on the solid phase and the concentration of F in solution when both phases are in equilibrium. To analyze the experimental data and describe equilibrium state in adsorption between solid and liquid phases, Langmuir and Freundlich, isotherm models were used. The curve related to each equilibrium and investigations of the model correlation coefficient (R^2) with experimental results show to what extent they follow each model.[37] The adsorption isotherm parameters were estimated using the model equations stated in Table 2.

Table 2. The equation of isotherm models employed for F− adsorption[38, 39]

Model	Main equation	Linear Form	Plot
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	$\log(q_e) = \log(K_f) + \frac{1}{n}\log(C_e)$	log q_e vs log C_e
Langmuir	$q_e = \dfrac{q_m k_1 C_e}{1 + K_1 C_e}$	$\dfrac{C_e}{q_e} = \dfrac{C_e}{q_m} + \dfrac{1}{q_m K_L}$	C_e/q_e vs C_e

Kinetics of the adsorption process: Adsorption kinetics are used to determine the mechanisms of controlling adsorption processes including adsorption, chemical reaction, and diffusion mechanisms and for describing the behavior of transfer of adsorbate molecules per unit of time or for investigating the variables affecting the reaction rate.[40]

In first-order kinetic model (Lagergren), it is assumed that the rate of changes in withdrawal of the solute over time is directly in proportion to variations in the saturation concentration and the amount of adsorbent withdrawal with time. First-order linear kinetics is shown in Equation 3. In second-order kinetic model (Ho), it is assumed that adsorption process can be controlled by chemical adsorption as shown in Equation 4.[41, 42]

$$Log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad \text{.................................. Equation 3}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad \text{...................................Equation 4}$$

The experiments to determine the adsorption isotherms and kinetics were performed with an adsorbent amount of 0.02 g/L and F concentration of 20 mg/L at pH 6. The estimated adsorption isotherm and kinetics parameters are presented in Table 3.

Table 3. Kinetic data for the sorption of fluoride (F) on ZnO NPs [C_0=initial concentration of fluoride (mg/L); R^2=correlation coefficient; K_1 and K_2=rate constants of adsorption (min^{-1}) in the Lagergren and Ho models, respectively; q_e=amount of fluoride adsorbed at equilibrium (mg/g)]

C_0 (mg/L)	Lagergren			Ho		
	R^2	K_1	q_e	R^2	K_2	q_e
15	0.462	0.009	0.77	0.998	0.2	2.25
20	0.516	0.0094	0.97	0.999	0.047	4.65
30	0.6	0.015	0.068	0.99	0.01	8.78
40	0.61	0.012	0.158	0.475	1e-8	10000

According to the obtained results, the removal of F on ZnO NPs followed the Ho kinetic model with correlation coefficient (R^2) of 0.999 at 20 mg/L, suggesting that the rate-limiting step is a chemical adsorption (Table 3).[43]

The isotherm data fitted into the Langmuir isotherm at all concentrations, which indicates a monolayer adsorption on a homogeneous surface (Table 4).[42,43]

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538 Research report
    Fluoride 53(3 Pt 2):531-541
    July-September 2020

Fluoride removal from aqueous solutions by zinc oxide nanoparticles   538
Mahvi, Rahdar, Igwegbe, Rahdar, Ahmadi

Table 4. Isotherm data for the sorption of fluoride (F) on ZnO NPs [C_0=initial concentration of fluoride (mg/L); R^2=correlation coefficient; K_F and K_L=Freundlich and Langmuir constants related to adsorption capacity; q_m=maximum adsorption capacity (mg/g)]

C_0 (mg/L)	Freundlich			Langmuir		
	R^2	K_F	q_e	R^2	K_L	q_e
15	0.984	2.057	0.125	0.9993	1.95	16.6
20	0.974	4.6	0.043	0.9998	4.5	100
30	0.99	10.23	0.173	0.9992	7.19	2.27
40	0.643	8.59	0.129	0.9995	9.2	2.1

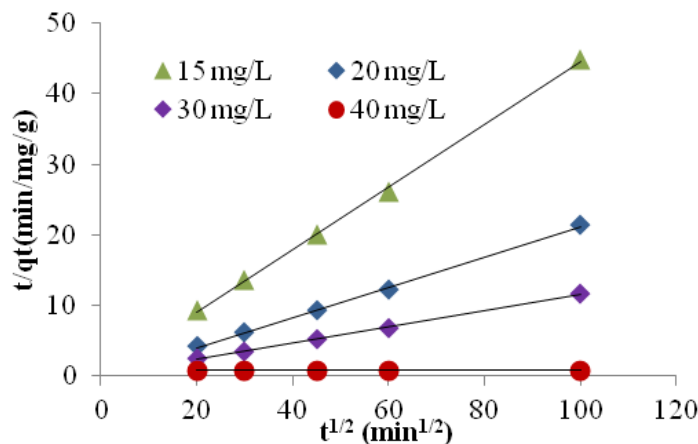Figure 5 shows the adsorption kinetic (Ho) plot for F removal on ZnO NPs.

Figure 5. Pseudo second order (Ho) kinetic plot for fluoride (F) removal on ZnO NPs.

CONCLUSION

In this research we investigated the efficacy of zinc oxide nanoparticles (ZnO NPs) as an adsorbent for the elimination of fluoride (F) from aqueous solutions. The effects of pH, contact time, initial F concentration, and adsorbent dosage on the removal of F from aqueous solutions on ZnO NPs were examined. Langmuir and Freundlich adsorption isotherms were applied to fit the adsorption experimental data. From the results, the adsorption efficiency was increased by increasing the pH from 3 to 6. The adsorption efficiency was increased as the contact time was increased. It was also found that with increasing amount of ZnO NPs adsorbent, the removal efficiency decreased. Maximum F removal was achieved at 60 min, at pH 6, with an adsorbent dosage of 0.02 g/L, and an initial F concentration of 20 mg/L. These optimum conditions of pH 6, adsorbent dose: 0.06 g/L, time: 60 min, and initial F

539   Research report
      Fluoride 53(3 Pt 2):531-541
      July-September 2020

Fluoride removal from aqueous solutions by zinc oxide nanoparticles   539
Mahvi, Rahdar, Igwegbe, Rahdar, Ahmadi

concentration: 20 mg/L gave an efficiency of 97.5%. The results revealed that the experimental data fits the pseudo-second-order (Ho) kinetic (R^2 = 0.9999 at 20 mg/L F concentrations) and Langmuir isotherm (R^2 = 0.999) models. Based on the data obtained in this study, it can be concluded that the adsorption of F by ZnO NPs is an efficient and reliable method for F removal from liquid solutions.

ACKNOWLEDGMENTS

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540   Research report
      Fluoride 53(3 Pt 2):531-541
      July-September 2020

Fluoride removal from aqueous solutions by zinc oxide nanoparticles   540
Mahvi, Rahdar, Igwegbe, Rahdar, Ahmadi

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