

# FLUORIDE IONS REMOVAL EFFICIENCY OF NATURAL/ACTIVATED ZEOLITE AND BENTONITE SORBENTS

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*Addressing the health concern of fluoride ions contamination in water, that cause such deceases as dental and skeletal fluorosis, requires the development of effective adsorption materials for water treatment. Our research objective was to evaluate the adsorption properties and capacities of zeolite and bentonite, sourced from Ukrainian deposits, and their acid-activated forms in relation to fluoride ions and estimate fitting this data to various adsorption models. Characterization of natural and acid-activated zeolite and bentonite sorbents was performed through X-ray diffraction to determine the phase composition of these substances. Adsorption experiments were carried out at different initial fluoride ions concentrations (3, 5, 10 and 15 mg/l) and pH (3.7; 7.5). Acidification (changing pH from 7.5 to 3.7) increase adsorption capacity of natural zeolite and bentonite more than twice. It was found that natural zeolite removes fluoride ions at the level of 67 % at pH 3.7 and a high dosage of sorbent – 10 g/l and an initial concentration of fluoride ions – 5 mg/l, while its acid-activated form was more effective - the removal of fluoride ions is 86 % at a lower dosage of sorbent – 1 g/l. Similarly, natural bentonite demonstrated a maximum removal efficiency of 45 % at pH 3.7 and a dosage of sorbent – 10 g/l, and its acid-activated form allowed for the removal of fluoride ions of about 83 % at a dosage of sorbent – 2 g/l at the same fluoride ions concentration. It is shown that the Vagelar-Langmuir (VL) isotherm model is the most accurate for describing the process of fluoride ions adsorption by acid-activated forms of natural sorbents, where the R<sup>2</sup> values are close to 0.999, indicating monolayer adsorption on homogeneous active centers. The obtained results indicate the greater efficiency of acid-activated forms of natural sorbents and the prospects of their use for the removal of fluoride ions from water.*

**Keywords:** adsorption isotherm models, bentonite, fluoride ions adsorption, natural sorbents, water purification, zeolite

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## 1. Introduction

Fluoride ions, a naturally occurring element, is often found in the environment and can enter water sources through both natural processes and anthropogenic activities (Edmunds & Smedley, 2013). While fluoride ions at low concentrations have beneficial effects, particularly in preventing dental caries, its presence at higher levels in drinking

water is a major global health concern, leading to conditions like dental and skeletal fluorosis (Tiwari et al., 2023). Therefore, the removal of excess fluoride ions from water sources is not just a scientific challenge but also a public health priority.

Several methods are used for this purpose, including precipitation (Ho et al., 2023; Lacson et al., 2022; Xia et al., 2021), membrane processes (Huang et al., 2023; Koli et al., 2023), electrocoagulation (Castañeda et

al., 2023; Tashauoei et al., 2023), adsorption (Dar & Kurella, 2023; He et al., 2020), and ion exchange (Yu et al., 2021), each with their unique advantages and limitations (Kurylenko et al., 2023). Precipitation methods, like utilizing lime (Atia & Hoggui, 2015) or calcium hydroxide or other calcium salts (Atia & Bebbba, 2013) are established and cost-effective but generate significant amount of sludge, demanding proper disposal. Ion exchange processes (Yu et al., 2021) offer high efficiency but involve high operational costs and require regeneration or replacement of expensive resins. Membrane filtration techniques, such as reverse osmosis (Huang et al., 2023), are also effective but require high operational costs and energy consumption and are sensitive to membrane fouling. Among these, adsorption emerges as a particularly promising method (Dar & Kurella, 2023) due to its simplicity, cost-effectiveness, and the variety of adsorbents that can be used. In the adsorption process, fluoride ions are accumulated on the surface of a solid material or adsorbent, leading to an effective reduction in the fluoride ions concentration in water (Dar & Kurella, 2023). Natural sorbents, such as bentonite (Kalsido et al., 2021) and zeolite (Wirtu et al., 2021), are especially attractive in this context due to their abundance, low cost, and environmental friendliness. These materials are not only naturally available and cost-effective but also show great potential in large-scale water purification applications. Moreover, the adsorption efficiency of these natural sorbents can be significantly enhanced through various activation or modification processes (Samatya et al., 2007; Wirtu et al., 2021; Yang et al., 2022). These processes aim to increase the number of active sites or alter the surface properties of the sorbents, thereby

improving their capacity to adsorb fluoride ions.

This research aims to investigate and evaluate the adsorption properties of natural sorbents, as well as their activated forms, for the efficient removal of fluoride ions from water and fitting this data to various adsorption models to understand the interaction mechanisms.

## 2. Materials and Methods

Two natural sorbents from Ukrainian sources were utilized: zeolite, obtained from the Sokyrnytsia deposit and bentonite, extracted from the Cherkasy deposit. The chemical compositions of these materials that are useful for understanding their adsorptive properties, are described in appended Table 1, natural zeolite was labelled as Zeo-0 and natural bentonite as Bent-0.

**Table 1.** Chemical composition of Zeo-0 (The Chemical Composition of the Zeolite / Description Products, n.d.) and Bent-0 (Chuprinov et al., 2019)

Component	Zeo-0	Bent-0
SiO <sub>2</sub>	65.0 - 71.3%	44.43 - 54.84%
Al <sub>2</sub> O <sub>3</sub>	11.5 - 13.1%	14.69 - 31.49%
CaO	2.7 - 5.2%	0.41 - 2.11%
K <sub>2</sub> O	2.2 - 3.4%	0.06 - 3.4%
Fe <sub>2</sub> O <sub>3</sub>	0.7 - 1.9%	4.69 - 10.99%
MgO	0.6 - 1.2%	0.1 - 1.68%
Na <sub>2</sub> O	0.2 - 1.3%	0.03 - 1.09%
TiO <sub>2</sub>	0.1 - 0.3%	0.28 - 0.8%
MnO	0.04%	0.01 - 0.22%
P <sub>2</sub> O <sub>5</sub>	0.02%	0.01 - 0.23%
Si/Al:	4.8 - 5.4	1.5 - 3.3

As a sorbent activation method was used acid activation: This involved treating the sorbents with a 2M HNO<sub>3</sub> solution. Here, 30 g of the sorbent was added in 350 ml of the solution for period of 4 hours with intense stirring. Following this, the sorbent was washed using vacuum filtration and rinsing 3 times with distilled water and subsequently dried. Thus, four samples were investigated as sorbents for the absorption of fluoride ions: natural zeolite (Zeo-0), acid-activated zeolite (Zeo-1), natural bentonite (Bent-0), and acid-activated bentonite (Bent-1).

X-ray diffraction (XRD) measurements were performed using a Rigaku Ultima-IV diffractometer.

The adsorption experiments were methodically designed, employing these sorbents across a spectrum of initial fluoride ions concentrations (3, 5, 10, and 15 mg/l). These concentrations were chosen to mirror the fluoride ions levels typically found in both natural and municipal water systems in Ukraine. Additionally, the experiments were conducted across a range of pH levels (3.7; 7.5) to assess the sorbents' performance under varying acidic and neutral conditions.

The experiments also carefully considered the sorbent dosage, varying from 0.25 g/l to 10 g/l of the model solution. This range was chosen to determine the optimal amount of sorbent required for maximum fluoride ions removal efficiency.

Concentration of fluoride ions was measured by potentiometric analysis commenced with the separation of the adsorbent from the solution following the adsorption process. Upon separation, an ionic-strength adjustment buffer (ISAB) was introduced to each sample to maintain a consistent ionic environment, thereby optimizing conditions for accurate fluoride

ions detection. The analysis was then conducted using the ЭЛИТ-221 fluoride ions-selective electrode paired with the И-160МН ion meter.

For all experiments, plastic containers were used to avoid any potential interactions of fluoride ions with glass materials. To ensure uniformity in the adsorption process was employed a shaker.

The calculation of research results was carried out according to the following formulas:

$$\alpha = \left(1 - \frac{C_e}{C_0}\right) \cdot 100\%, \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \cdot V_{\text{solution}}}{m_{\text{adsorbent}}}, \quad (2)$$

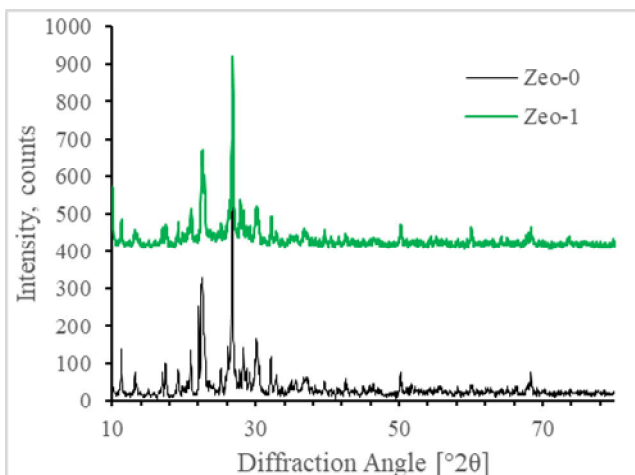
where  $\alpha$  is removal efficiency, %;  $C_0$  is initial concentration of fluoride ions in solution;  $C_e$  – equilibrium concentration of fluoride ions;  $q_e$  – adsorption capacity of adsorbent.

### 3. Results and Discussion

The XRD patterns of Zeo-0 (natural zeolite) and Zeo-1 (acid activated zeolite), when compared, exhibit minor differences in intensity and the presence of certain peaks, indicating low structural and compositional changes due to acid activation (Fig. 1).

For Zeo-0, the major phase identified is clinoptilolite-Na with a quantified value of 73.7 %, and the minor constituents include quartz (SiOp3-221) and traces of cristobalite. Post-acid activation, the clinoptilolite-Na phase in Zeo-1 decreases marginally to 69.6 %, indicating that the structure remains predominantly clinoptilolite-Na but with a slightly reduced quantity. The quartz content has also a slight decrease, as shown by the phase quantity of 30.4 % in Zeo-1 compared to 23.2 % in Zeo-0, and the cristobalite phase is no longer detected in Zeo-1. These results

suggest that acid activation has a minor effect on phases and predominantly affect active sites of adsorbent. Statistical parameters, such as  $R_{wp}$  (Weighted Pattern Residual) that is a measure of the fit between the observed and calculated diffraction patterns and  $\chi^2$  (Chi-squared) that is a statistical parameter used to assess the goodness of fit of the observed data to the model (the closer these parameters are to 1, the better the fit they suggest) were used to describe a goodness of fit for both Zeo-0 and Zeo-1 set of data. Zeo-0 and Zeo-1 have  $R_{wp}$  values of 22.59 and 23.43, respectively. The  $\chi^2$  values for both samples are close to 1 (Zeo-0: 1.6016; Zeo-1: 1.6664), suggesting acceptable fits for the phase quantification models used.

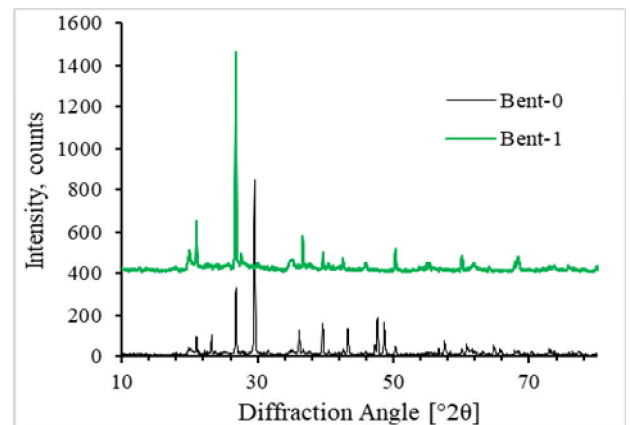


**Fig. 1.** XRD patterns of natural and activated zeolites

Thus, the acid activation of natural zeolite results in subtle yet discernible changes in the XRD patterns, with a slight decrease in the clinoptilolite content and the absence of the cristobalite phase.

The comparative analysis of XRD patterns for natural bentonite (Bent-0) and its acid-activated form (Bent-1) reveals several notable differences (Fig. 2). In the natural bentonite, the quantified phase compositions

include  $\text{SiO}_2$  (quartz), kaolinite, and calcite, with respective values of 15.1 %, 41 %, and 44 %. Post-acid treatment, there is a significant increase in the quartz content – 28 % and a substantial rise in the kaolinite phase 71 %, while the calcite phase is completely eliminated – 0.6 %.



**Fig. 2.** XRD patterns of natural and activated bentonites

The increase in the quartz and kaolinite content suggests that these phases are more resistant to acid dissolution compared to calcite. The overlay of the XRD patterns from both samples further illustrates these changes. Simultaneously, the prominence of the peaks ascribed to quartz and kaolinite in the activated sample underpins the quantitative results, indicating the enrichment of these phases after the acid treatment. Statistically, the  $R_{wp}$  values indicate a modest increase from 25.65 to 28.45 post-activation, while the Chi-squared value also increases, suggesting that the acid activation may introduce some amorphization or decrease the crystallinity of the bentonite. In concluding, acid activation of bentonite using  $\text{HNO}_3$  significantly alters its mineralogical composition, predominantly by removing calcite and concentrating quartz and kaolinite.

The study of adsorption efficiency of natural zeolite and bentonite at dosage of 10 g/l for fluoride ions removal under various conditions was carried out (Table 2). In this study were estimated such parameters of adsorbent effectiveness as  $q_e$  (equilibrium adsorption capacity of adsorbent) and  $\alpha$  (removal efficiency).

**Table 2.** Fluoride ions adsorption using Zeo-0 and Bent-0 sorbents

Sorbent Type	pH	$C_0$ , mg/l	$\alpha$ , %	$q_e$ , mg/g
Zeo-0	7.5	3	13.7	0.4
		5	22.4	1.1
		10	16.4	1.6
		15	25.1	3.8
	3.7	3	56.3	1.7
		5	66.8	3.3
		10	56.4	5.6
		15	51.3	7.7
Bent-0	7.5	3	8.3	0.3
		5	16.0	0.8
		10	18.0	1.8
		15	12.0	1.8
	3.7	3	31.7	1.0
		5	35.2	1.8
		10	44.5	4.5
		15	44.1	6.6

As can be seen from the data presented in Table 2, for zeolite at neutral pH (7.5), the fluoride ions removal efficiency increases with the initial fluoride ions concentration, starting from 13.7 % at 3 mg/l and peaking at 25.1 % at 15 mg/l. At acidic pH (3.7), zeolite shows a very high fluoride ions removal efficiency, starting at 56.3 % for 3 mg/l and reaching the highest efficiency of 66.8 % at 5 mg/l, then decreasing to 51.3 % at 15 mg/l.

For bentonite, both at a neutral pH 7.5 and at pH 3.7, the fluoride ions removal

efficiency ( $\alpha$ ) initially increases as the initial fluoride ions concentration ( $C_0$ ) grows from 3 mg/l with an  $\alpha$  value of 8.3 % for pH 7.5 and 31.7 % for pH 3.7, reaching its peak efficiency at 10 mg/l with an  $\alpha$  value of 18 % for pH 7.5 and 44.5 % for pH 3.7. Beyond this peak, at 15 mg/l, the efficiency declines to 12 % for pH 7.5 and 44 % for pH 3.7, suggesting that the adsorption sites are approaching saturation and cannot bind additional fluoride ions as effectively.

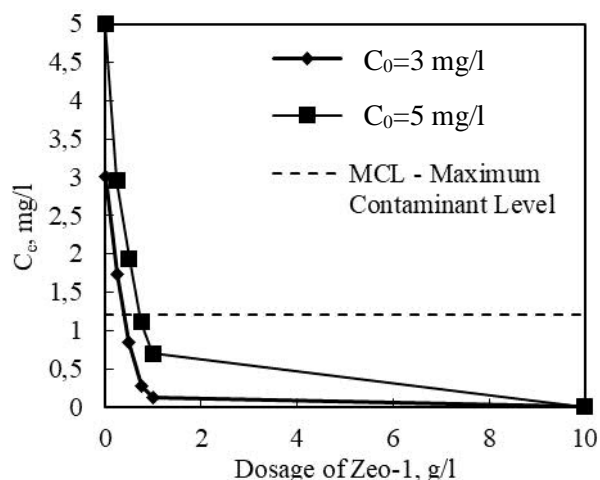
The fluoride ions removal efficiency of both zeolite and bentonite is dependent on the initial concentration of fluoride ions and is significantly influenced by the pH of the solution. Acidification improves the performance of both sorbents, with zeolite showing exceptionally high efficiency at lower concentrations. The highest  $q_e$  values were 7.7 for Zeo-0 and 6.6 for Bent-0 at  $C_0$  of 15 mg/l.

Were also conducted studies to determine the influence of sorbent dosage using zeolite (Fig. 3) at initial fluoride ions concentrations of 3 mg/l and 5 mg/l, with varying sorbent masses: 0.25 g/l, 0.5 g/l, 0.75 g/l, 1 g/l, and 10 g/l. In Figure 3, the dashed line represents the Maximum Contaminant Level (MCL) for fluoride ions in Ukraine, which is set at 1.2 mg/l. It was interpolated that a sorbent dose of 0.4 g/l was required to achieve the standard fluoride ions concentration at an initial concentration of 3 mg/l, and 0.7 g/l at 5 mg/l.

The adsorption efficiency of zeolite increased with higher dosages but not linearly. For example, at an initial fluoride ions concentration of 3 mg/l, the adsorption efficiency at 0.25 g/l dose was over 40 %, which increased to nearly 96 % at 1 g/l.

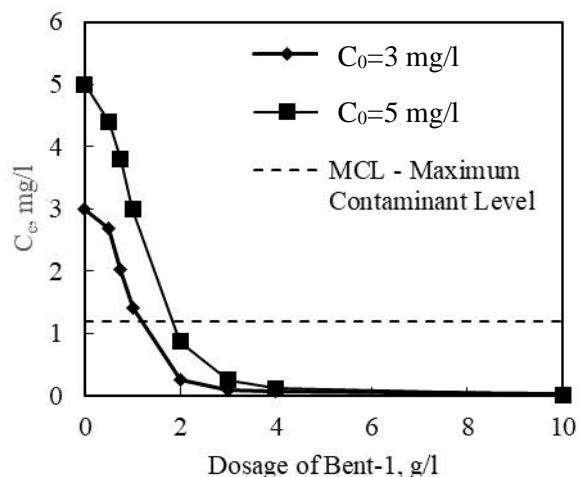
This indicates that even a small dose of sorbent can lead to high contaminant removal,

but as the initial fluoride ions concentration increases to 5 mg/l, the required sorbent dose for a similar removal percentage also increases.



**Fig. 3.** The residual concentration of fluoride ions by Zeo-1 with different dosages

A similar study was conducted for bentonite (Fig. 4) with the same initial fluoride ions concentrations. The sorbent dosages were adjusted to 0.5 g/l, 0.75 g/l, 1 g/l, 2 g/l, 3 g/l, 4 g/l, and 10 g/l.



**Fig. 4.** The residual concentration of fluoride ions by Bent-1 with different dosages

The results indicated that the MCL was only achieved using bentonite at a dosage of 1.18 g/l for an initial fluoride ions concentration of 3 mg/l and 1.84 g/l for 5 mg/l.

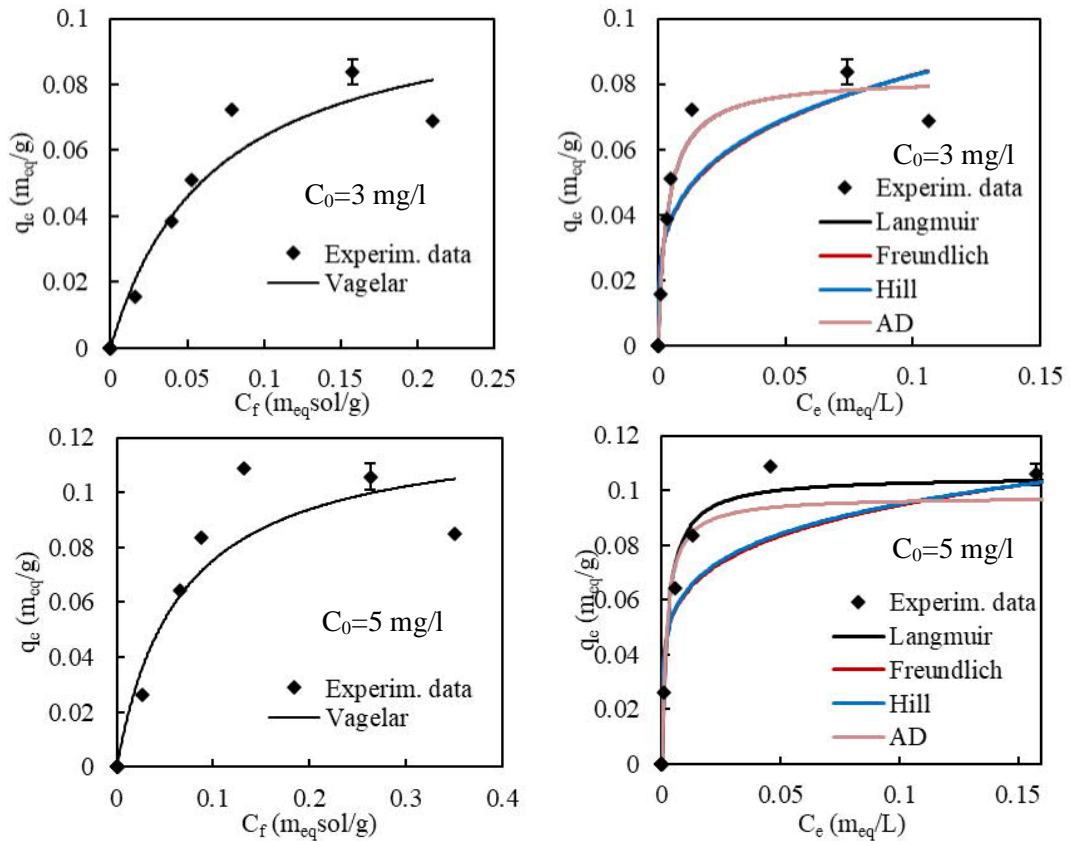
The graph illustrates that beyond the intersection points, additional increases in bentonite dosage continue to reduce fluoride ions concentration, but with diminishing efficiency.

Overall, the optimal sorbent dosage for both initial fluoride ions concentrations appear to be around 2 g/l, where fluoride ions levels are safely below the MCL, offering a balance between efficiency and sorbent usage.

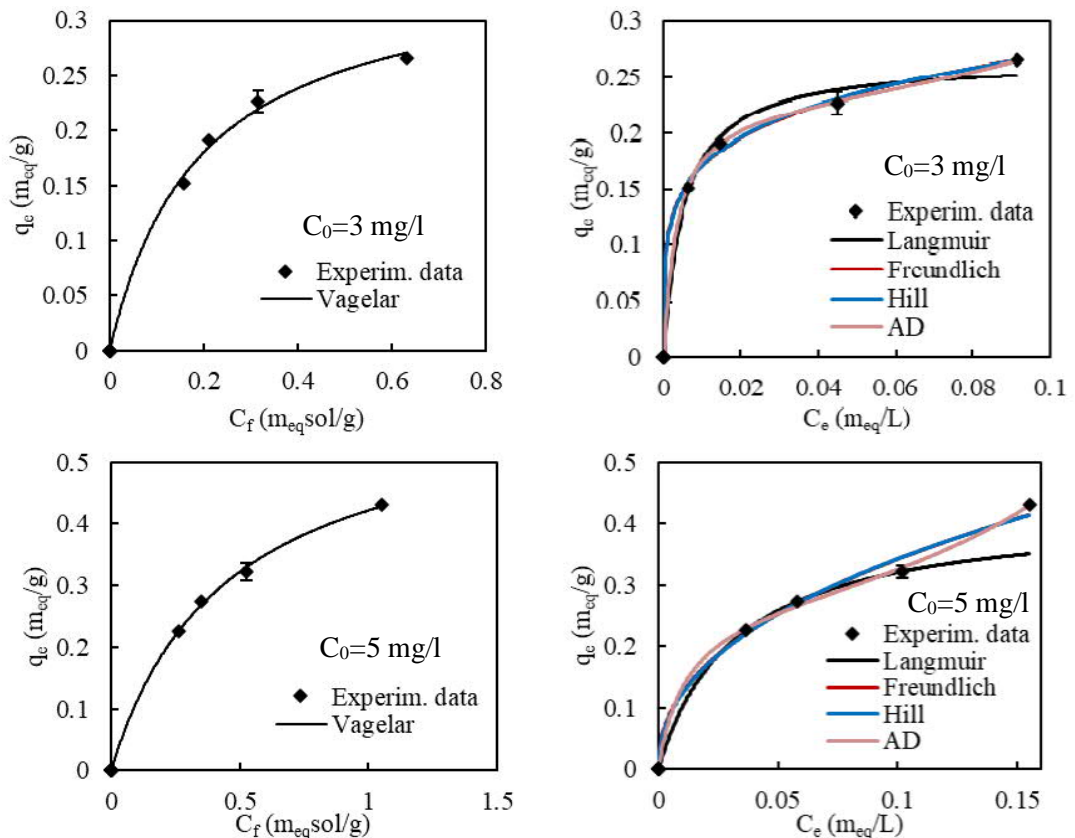
In summary, this comparative analysis between zeolite and bentonite underscores the nuanced interplay between sorbent dosage and fluoride ions removal efficacy, highlighting that while both sorbents exhibit enhanced performance with increased dosages, there exists an optimal dosage range that ensures maximum efficiency – at  $C_0 = 3$  mg/l for zeolite 0.4 g/l and for bentonite – 1.2 g/l and at  $C_0 = 5$  mg/l for zeolite 0.7 g/l and for bentonite – 1.8 g/l.

We investigated the adsorption capacity of zeolite for fluoride ions at concentrations of 3 mg/l and 5 mg/l and utilize this experimental data for various isotherm models fitting (Fig. 5) to understand the adsorption mechanisms. The models analyzed included Vagelar-Langmuir (VL), Langmuir, Freundlich, Hill, and Aranovich-Donohue (AD) (Al-Ghouti & Da'ana, 2020). Same set of isotherm models for describing fluoride ions adsorption on bentonite (Fig. 6).

The Vagelar-Langmuir (VL) model is an adsorption isotherm model employed to describe the relationship between the amount of adsorbate (fluoride ions) adsorbed onto a solid surface (zeolite or bentonite) and the equilibrium concentration of the adsorbate remaining in the solution. Similar to the Langmuir model, it assumes monolayer adsorption on a homogeneous surface with no interaction between adsorbed molecules.



**Fig. 5:** Isotherm models for fluoride ions adsorption on Zeo-1



**Fig. 6:** Isotherm models for fluoride ions adsorption on Bent-1

**Table 3.** Statistical analysis of Zeo-1 isotherm models

Isotherm Model	C <sub>0</sub> (mg/l)	R <sup>2</sup>	SEy	F-test	Model Parameter 1	Model Parameter 2
VL	3	0.999	0.022	0.994	K <sub>L</sub> =0.19	q <sub>max</sub> =0.45
VL	5	0.999	0.012	0.999	K <sub>L</sub> =0.35	q <sub>max</sub> =0.61
Langmuir	3	0.998	0.001	0.987	K <sub>L</sub> =196	q <sub>max</sub> =0.27
Langmuir	5	0.999	0.001	0.662	K <sub>L</sub> =31	q <sub>max</sub> =0.42
Freundlich	3	0.999	0.016	0.997	k <sub>F</sub> =0.43	n=0.93
Freundlich	5	0.998	0.035	0.983	k <sub>F</sub> =5	n=2.29
Hill	3	0.999	0.0221	0.997	K <sub>D</sub> =196	q <sub>max</sub> =1.76
Hill	5	0.998	0.051	0.982	K <sub>D</sub> =31	q <sub>max</sub> =5.26
AD	3	0.999	0.006	0.999	K <sub>L</sub> =310	q <sub>max</sub> =0.23
AD	5	0.999	0.020	0.998	K <sub>L</sub> =91	q <sub>max</sub> =0.27

**Table 4.** Statistical analysis of Bent-1 isotherm models

Isotherm Model	C <sub>0</sub> (mg/l)	R <sup>2</sup>	SEy	F-test	Model Parameter 1	Model Parameter 2
VL	3	0.983	0.044	0.854	K <sub>L</sub> =0.07	q <sub>max</sub> =0.11
VL	5	0.951	0.064	0.789	K <sub>L</sub> =0.07	q <sub>max</sub> =0.13
Langmuir	3	0.962	0.002	0.924	K <sub>L</sub> =261	q <sub>max</sub> =0.08
Langmuir	5	0.976	0.002	0.862	K <sub>L</sub> =397	q <sub>max</sub> =0.11
Freundlich	3	0.535	0.073	0.740	k <sub>F</sub> =0.15	n=3.85
Freundlich	5	0.512	0.075	0.768	k <sub>F</sub> =0.14	n=5.51
Hill	3	0.557	0.083	0.744	K <sub>D</sub> =261	q <sub>max</sub> =0.81
Hill	5	0.534	0.084	0.777	K <sub>D</sub> =397	q <sub>max</sub> =0.61
AD	3	0.711	0.035	0.924	K <sub>L</sub> =260	q <sub>max</sub> =0.09
AD	5	0.847	0.045	0.915	K <sub>L</sub> =497	q <sub>max</sub> =0.1

However, Vagelar model could not be directly compared with the other isotherm models because VL model utilizes the driving force ( $C_f$  – equilibrium concentration in milliequivalents per gram ( $m_{eq}/g$ ) of adsorbent), a ratio of the liquid phase concentration to the solid phase loading, as the independent variable. This contrasts with the traditional concentration ( $C_e$  – equilibrium concentration in the solution in milliequivalents per liter ( $m_{eq}/l$ )) used by the Langmuir, Freundlich, Hill, and AD models.

Vagelar-Langmuir (VL): This model postulates a relationship between the driving force ( $C_f$ ) and the amount adsorbed ( $q_e$ ) through the following equation:

$$q_e = \frac{C_f \cdot q_{max}}{C_f + K_{LV}}, \quad (3)$$

where  $q_e$  - amount of fluoride ions adsorbed per gram of adsorbent ( $m_{eq}/g$ ),  $C_f$  - maximum driving force ( $m_{eq}/g$ ),  $q_{max}$  - equilibrium concentration in the solution ( $m_{eq}/l$ ),  $K_{LV}$  - Langmuir-Vagelar constant ( $L/m_{eq}$ ) related to the affinity of fluoride ions for the adsorbent sites.

Langmuir: this widely used model assumes monolayer adsorption on a homogenous surface with no interaction between adsorbed molecules. It is described by the following equation:

$$q_e = \frac{K_L \cdot q_{max} \cdot C_e}{1 + K_L \cdot C_e}, \quad (4)$$



where  $q_e$  - amount of fluoride ions adsorbed per gram of adsorbent ( $m_{eq}/g$ ),  $q_{max}$  - maximum adsorption capacity of the adsorbent ( $m_{eq}/g$ ),  $K_L$  - Langmuir constant ( $L/m_{eq}$ ),  $C_e$  - equilibrium concentration of fluoride ions in the solution ( $m_{eq}/l$ ).

Freundlich: this model applies to heterogeneous surfaces and multilayer adsorption. It is represented by the following equation:

$$q_e = k_F \cdot C_e^{1/n}, \quad (5)$$

where  $q_e$  - amount of fluoride ions adsorbed per gram of adsorbent ( $m_{eq}/g$ ),  $K_f$  - Freundlich constant ( $m_{eq}/g \cdot (L/m_{eq})^n$ ),  $n$  - Freundlich exponent,  $C_e$  - equilibrium concentration of fluoride ions in the solution ( $m_{eq}/l$ ).

Hill: this model delves deeper into the interaction between adsorbed molecules. Unlike Langmuir's assumption of no interaction, the Hill model considers cooperative binding, where the adsorption of one molecule can influence the subsequent adsorption of others. This cooperativity is reflected by the Hill coefficient ( $h$ ) in the formula. Here's a simplified representation of the Hill model formula:

$$q_e = \frac{q_{max} \cdot C_e^a}{K_D^a + C_e^a}, \quad (6)$$

where  $q_e$  - amount of fluoride ions adsorbed per gram of adsorbent ( $m_{eq}/g$ ),  $q_{max}$  - maximum adsorption capacity of the adsorbent ( $m_{eq}/g$ ),  $C_e$  - equilibrium concentration of fluoride ions in the solution ( $m_{eq}/l$ ),  $a$  - Hill cooperativity coefficient of the binding interaction.

Aranovich-Donohue: unlike the Langmuir and Vagelar-Langmuir models, which assume homogeneous surfaces, the AD model accounts for both surface heterogeneity and energetic heterogeneity. It is described by the following equation:

$$q_e = \frac{q_{max} \cdot K_L \cdot C_e}{(1 + K_L \cdot C_e) \cdot \left(1 + \frac{C_e}{C_0}\right)^n}, \quad (4)$$

where  $q_e$  - amount of fluoride ions adsorbed per gram of adsorbent ( $m_{eq}/g$ ),  $q_{max}$  - maximum adsorption capacity of the adsorbent ( $m_{eq}/g$ ),  $K_L$  - Langmuir constant ( $L/m_{eq}$ ),  $C_e$  - equilibrium concentration of fluoride ions in the solution ( $m_{eq}/l$ ),  $C_0$  - initial concentration of fluoride ions in the solution ( $m_{eq}/l$ ).

In Table 3 are presented statistical parameters to determine the most accurate model for fluoride ions adsorption using Zeo-1, Table 4 presented data for Bent-1.

The VL isotherm model, known for its basis in monolayer adsorption on a homogeneous surface, displays near-perfect  $R^2$  values of 0.999 for an initial fluoride ions concentration of 3 mg/l and 0.999 for 5 mg/l for Zeo-1 and 0.983 and 0.951 for the respective concentrations of Bent-1, highlighting its high predictive accuracy. These  $R^2$  values are indicative of the model's ability to represent the adsorption process with minimal deviation from the observed data. The VL model's parameters, specifically the adsorption affinity constant  $K_L$  and the maximum adsorption capacity  $q_{max}$ , increased with the initial fluoride ions concentration.  $K_L$  shifted from 0.19 at 3 mg/l to 0.35 at 5 mg/l for Zeo-1 and for Bent-1  $K_L$  is equal 0.07 for both  $C_0$ ,  $q_{max}$  changed from 0.45 mg/g to 0.61 mg/g for Zeo-1 and from 0.11 mg/g to 0.13 mg/g for Bent-1. These increases align with the model's postulates, suggesting that with a higher concentration of fluoride ions in the solution, the adsorbent's affinity for fluoride ions enhances, and the total adsorption capacity expands, leading to more effective utilization of available adsorption sites.

The Langmuir model, which also assumes monolayer adsorption but has different approach to adsorption equilibrium and kinetics, similarly exhibits high  $R^2$  values, particularly 0.998 for  $C_0$  of 3 mg/l and 0.999 for 5 mg/l for Zeo-1 and 0.962 and 0.976 for the respective concentrations of Bent-1. The Langmuir constants  $K_L$  and  $q_{max}$  increase with concentration, which may indicate a stronger affinity and greater adsorption capacity at higher fluoride ions levels.

The Freundlich model, applicable to heterogeneous surfaces, shows  $R^2$  values of 0.999 and 0.998 for Zeo-1 and 0.535 and 0.512 for Bent-1, which are lower for Bent-1 compared to the VL and Langmuir models. This suggests a moderate fit to the experimental data, reflecting the complexity of adsorption on a non-uniform surface. The Freundlich constants  $k_F$  and  $n$  differ slightly between the concentrations, with  $n$  increasing, which could suggest a higher heterogeneity or complexity in the adsorption process at higher concentrations.

The Hill model, considering cooperative adsorption, presents shows the same trend as Freundlich model with apparently high  $R^2$  values (0.999 and 0.998) for zeolite and low values for bentonite (0.557 and 0.534). The  $K_D$  values, akin to the Langmuir constant  $K_L$ , and  $q_{max}$  are significantly higher for the 3 mg/l concentration, suggesting that the cooperative adsorption mechanism may be more pronounced at this lower fluoride ions level.

Lastly, the Aranovich-Donohue (AD) isotherm, which takes into account adsorption on heterogeneous surfaces and potential multilayer adsorption, shows near-perfect  $R^2$  values of 0.999 for both concentrations for Zeo-1 and an increase in  $R^2$  from 0.71 to 0.847 with increasing fluoride ions concentration for Bent-1. This improvement

in  $R^2$  for Bent-1 may suggest that the AD model is better suited to capture the adsorption behavior at higher concentrations, potentially due to its consideration of multilayer adsorption.

In conclusion, the Vagelar-Langmuir model stands out with the highest  $R^2$  values both for Zeo-1 and Bent-1, suggesting it is the most reliable for describing fluoride ions adsorption under the tested conditions. In comparing the adsorption behavior of zeolite and bentonite through various isotherm models, we observe distinct differences in model fitting, reflective of the intrinsic properties and mechanisms of the two sorbents. Zeolite typically exhibits higher adsorption capacities, as indicated by greater  $q_{max}$  values across most models.

#### 4. Conclusions

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The study explored the efficiency of natural sorbents, specifically bentonite and zeolite, from Ukrainian deposits in removing fluoride ions from water. The research investigated the effects of initial fluoride ions concentrations, pH levels, adsorbent doses, and the impact of acid activation on the adsorption capabilities of these sorbents.

Key findings include investigations of different adsorption efficiencies of bentonite and zeolite at various pH levels and fluoride ions concentrations, with zeolite showing particularly high efficiency under acidic conditions, peak efficiency of fluoride ions removal for zeolite at neutral pH was 44.5 % and at pH 3.7 – 66.8 % and for bentonite - 18% and 25 % respectively. The optimal zeolite dosage for achieving desired fluoride ions removal to 1.2 mg/l was 0.4 g/l for initial concentration of fluoride ions  $C_0=3$  mg/l and 0.7 g/l for  $C_0=5$  mg/l, optimal

dosage of bentonite was 1.18 g/l and 1.84 g/l respectively.

Isotherm model fitting was conducted on the experimental data to understand the interaction mechanisms. Vagelar-Langmuir model stands out with the highest  $R^2$  values (0.999 for Zeo-1 and 0.983 for Bent-1), suggesting it is the most reliable for describing fluoride ions adsorption under the tested conditions. It provides a clear and consistent prediction of adsorption capacity across the studied concentration range.

In conclusion, acid-activated natural sorbents are very effective for fluoride ions removal and show a significant growth of effectiveness comparing to natural forms.

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## ЕФЕКТИВНІСТЬ ВИДАЛЕННЯ ФТОРУ ПРИРОДНИМИ/АКТИВОВАНИМИ ЦЕОЛІТНИМИ ТА БЕНТОНІТОВИМИ СОРБЕНТАМИ

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*Вирішення проблеми забруднення води іонами фтору, які спричиняють такі захворювання, як флюороз зубів та скелета, вимагає розробки ефективних адсорбційних матеріалів для очищення води. Метою нашого дослідження було оцінити адсорбційні властивості та ємність цеоліту і бентоніту, отриманих з українських родовищ, та їх кислотно-активованих форм по відношенню до іонів фтору, а також оцінити відповідність цих даних різним адсорбційним моделям. Експерименти з адсорбції проводили при різних початкових концентраціях фторид-іонів (3, 5, 10 і 15 мг/дм<sup>3</sup>) і рН (3,7; 7,5). Підкислення (зміна рН від 7,5 до 3,7) збільшує адсорбційну здатність природного цеоліту та бентоніту більш ніж удвічі. Встановлено, що природний цеоліт видаляє іони фтору на рівні 67 % при рН 3,7 та високому дозуванні сорбенту - 10 г/дм<sup>3</sup> і початковій концентрації іонів фтору - 5 мг/дм<sup>3</sup>, тоді як його кислотно активована форма виявилася більш ефективною - видалення іонів фтору становить 86 % при меншому дозуванні сорбенту - 1 г/дм<sup>3</sup>. Аналогічно, природний бентоніт продемонстрував максимальну ефективність видалення 45 % при рН 3,7 і дозуванні сорбенту 10 г/дм<sup>3</sup>, а його кислотно-активована форма дозволила видалити близько 83 % іонів фтору при дозуванні сорбенту 2 г/дм<sup>3</sup> при тій же концентрації іонів фтору. Показано, що модель ізотерми Вагелара-Ленгмюра є найбільш точною для опису процесу адсорбції фторид-іонів кислотно-активованими формами природних сорбентів, де значення R<sup>2</sup> близькі до 0,999, що свідчить про моношарову адсорбцію на однорідних активних центрах. Отримані результати свідчать про більшу ефективність кислотно-активованих форм природних сорбентів та перспективність їх використання для видалення фторид-іонів з води.*

**Ключові слова:** адсорбція фтору, бентоніт, моделі ізотерм адсорбції, очищення води, природні сорбенти, цеоліт