



# SYNTHESIS, CHARACTERIZATION AND APPLICATION OF CANCRINITE IN GROUND WATER TREATMENT FROM WADI EL-ASSIUTI AREA, ASSIUT-EGYPT.

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## ABSTRACT

Cancrinite is one of the rarest members of the feldspathoids group; it is classified also as a zeolite, due to its open pore structure, which confers molecular sieve properties. It was successively synthesized in the absence of organic template by hydrothermal method at 180°C for 5 days after stirring at high speed and aging in the synthesis mixture with the molar composition of  $1Na_2O: 6SiO_2: 1.6Al_2O_3: 9H_2O$ . The produced samples were investigated using X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR) and Thermo Gravimetric Analysis (TGA) DTA/TG. Cancrinite was tested as adsorbents for the removal of nitrate ions from the ground water samples from Wadi El-Assiuti–Egypt. The adsorption capacities of nitrate ions by cancrinite, as a function of its concentration, were determined at room temperature by varying the cancrinite concentration for each water samples. During the process, all the other parameters (pH and contact time) were kept constant with respect to the initial concentration of nitrate ions in the water samples. It was found cancrinite has good removal efficiency obtained at pH 6-7.6, adsorbent dosage 10 g/L, and contact time 60 min. The Langmuir constants model for  $NO_3^-$  ion sorption on the adsorption isotherms is fitted well. The  $R_L$  value in the present investigation was equal or less than one, indicating that the adsorption of  $NO_3^-$  ion by cancrinite is favorable.

**Keywords:** *Cancrinite, Ground water, Characterization, Element contents, Water treatment.*

## 1. INTRODUCTION

Groundwater refers to the water that is stored in the pervious, porous and permeable rocks referred to as aquifers, everywhere in the world. Depending on the rock type and formation, groundwater is found in the ground within the depth of 100 meters and in some places up to 1000 meters deep. A great percentage of people worldwide use this source of water for their agricultural, domestic and industrial

purposes (Press and Siever, 1985). Variation in groundwater chemistry is mainly a function of the interaction between the groundwater and the mineral composition of the aquifer materials through which it moves. Hydrochemical processes, including dissolution, precipitation, ion exchange, sorption, and desorption, together with the residence time occurring along the flow path, control the variation in chemical composition of groundwater (Apodaca et

al., 2002). Nitrate, due to its high water solubility, is possibly the most widespread groundwater contaminant in the world, seriously threatening supplies of drinking water and promoting eutrophication (Bhavnagar et al., 2011). A high concentration of nitrate in drinking water leads to production of nitrosamine, which is related to cancer and increases the risk of diseases such as methemoglobinemia in newborn infants (Bouwer, 1989; Samatya et al., 2006; Mažeikienė et al., 2008). Hence, reduction of nitrates in drinking water to permissible levels is mandatory for these reasons, the US Environmental Protection Agency (EPA) and the World Health Organization (WHO) have defined a maximum contamination level (MCL) of 10 mg N-NO<sub>3</sub>-L in water (US EPA, 2014), (WHO, 2007). Various technologies have been used to remove nitrate from groundwater, including reverse osmosis, ultrafiltration, ion exchange, ion-exchange-membrane bioreactors, catalytic reduction, electrodialysis, activated carbon, land disposal, chemical denitrification, and microbiological treatment (Santafé-Moros et al., 2005; Bhavnagar et al., 2011; Tofighy et al., 2012). Zeolites are crystalline hydrated aluminum silicates with a framework structure containing pores that are occupied by water and by alkali and alkaline earth cations. Due to their high cation-exchange ability as well as molecular sieve properties, natural zeolites (cheap materials, easily available in large quantities in many parts of the world) show special importance in water and gas purification, adsorption and catalysis (Inglezakis, 2005). Zeolites have also an advantage over filter

materials with significant permeability and are widely used for water purification by filtration (Sakalauskas 2003; Brannvall et al., 2006). Low-silica zeolites (LSZs) with Al/Si ratio of 1:1 like zeolite A (LTA), cancrinite (CAN) sodalite (SOD), zeolite P (GIS), zeolite X (FAU) and Nepheline Hydrate I (JBW) are relatively rare (Healey et al., 2000). These zeolites exhibit the highest ion exchange capacity and have important industrial applications. They are used as adsorbents or substitute for conventional phosphatic builder. Cancrinite-group minerals are framework aluminosilicates (feldspathoids) characterized by a network of (Al, Si) O<sub>4</sub> tetrahedral having fully ordered Al and Si cations. Their structure consists of parallel six-membered rings of alternating AlO<sub>4</sub> and SiO<sub>4</sub> tetrahedral (Jarchow 1965; Grundy and Hassan, 1982). The main objective of this study was to investigate the conversion of preparation of cancrinite under optimized synthesis conditions. In our study, it is aimed to putificate nitrate ions from ground water by adsorption on synthesized cancrinite and to investigate the kinetics and equilibrium parameters involved during this adsorption. The parameters in this study included initial concentration, contact time, temperature, adsorbent dosage and influence of pH. Moreover, our work is to investigate the features of nitrates ion sorption from ground water by using synthetic zeolite cancrinite under static and dynamic conditions.

## 2. HYDROGEOLOGICAL SETTING OF WADI ASSIUTI

Wadi EL-Assiuti area represents a segment of the Nile valley in Upper Egypt. It is located on the fringes of the flood plane east of Assiut city. The area is bounded by latitudes  $27^{\circ} 5' N$  and  $27^{\circ}20' N$  and longitudes  $31^{\circ}10' E$  and  $31^{\circ} 25' E$ . The area is located in an arid region with almost no rainfall. Temperature varies from  $5^{\circ} C$  in winter to  $45^{\circ}C$  in summer. El fatah district is a part of Wadi EL-Assiuti area in Assiut governorate from its eastern side Figs. (1a, b). Several studies were previously carried out on this study area for dealing with its

evaluation of its ground water potentiality. The study area is a rectangular flat area of about  $400 \text{ Km}^2$ . It is bounded from the west by the Nile River and from the other sides by the limestone plateau that is dissected by a great number of wadis. Groundwater in this aquifer is characterized by fresh water. The salinity from 800 to 1000 mg/L. The salt assemblages are:  $\text{Ca} (\text{HCO}_3)_2$ ,  $\text{Mg} (\text{HCO}_3)_3$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  which indicate a clear resemblance to the salt assemblages of surface water. The study of hydrochemical characteristics in Wadi EL-Assiuti revealed on the high concentration of nitrate in some studied wells relative to WHO (2004) and A.R.E (2007).

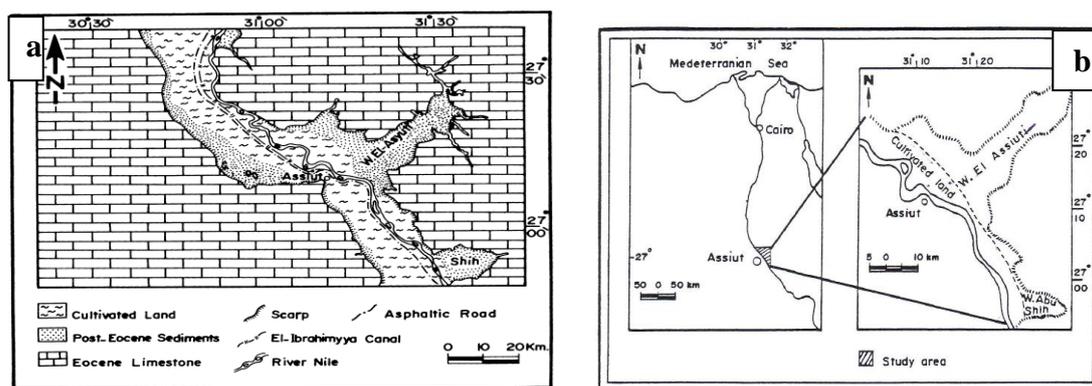


Fig. (1a, b): Simplified geological and Location map of Wadi EL-Assiuti

## 3. MATERIALS AND METHODS

Sodium Silicate (Aldrich),  $\text{NaAlO}_2$  (Sigma Aldrich), Sodium hydroxide (Aldrich), chemical reagents such as fumed silica (7 nm, Sigma Aldrich),  $\text{NaOH}$  (Merck, Darmstadt, Germany) and aluminum standard solution were used for zeolite synthesis. The various characteristics of the synthesized cancrinite were also identified include the FTIR spectra of the synthesized cancrinite that were obtained on a Shimadzu 2110 PC Scanning meter within the limits of  $4,000\text{--}500 \text{ cm}^{-1}$  with a resolution of  $0.5 \text{ cm}^{-1}$  (KBr pellets,

$\text{CAN/KBr} = 1/3$  by mass, 6 atm.). The X-ray diffractograms of the polymers were obtained with a Philips X-ray unit (Phillips generator PW-1710) and Ni-Filtered  $\text{CuK}\alpha$  radiations. TGA and DTG measurements were performed on a V 5.1 A Du Pont 2000 thermal analyzer at heating rate  $10^{\circ} C / \text{min}$  in air. The morphology of the polymers was examined by scanning electronic microscopy (SEM) using a Jeol JSM-5400 LV-ESM.

### 3.1. SYNTHESIS OF THE CANCRINITE

Cancrinite was prepared using cancrinite gel composition ( $6\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:30\text{SiO}_2:780\text{H}_2\text{O}$ ) and the synthesis mixture with the molar composition of  $\text{Na}_2\text{O}:\text{6SiO}_2:\text{1.6Al}_2\text{O}_3:\text{9H}_2\text{O}$ . Aluminum standard solution as the aluminum source was mixed with an aqueous solution of NaOH. Then sodium silicate was added to the mixture and the mixture was homogenized by stirring. Finally, the gel was transferred to a Teflon-lined autoclave and crystallization was carried out at  $180^\circ\text{C}$  under autogenously pressure without agitation for 24 h. The product was recovered by filtration, washed thoroughly with deionized water and dried at  $120^\circ\text{C}$  overnight.

### 3.2. CHARACTERIZATION OF SYNTHETIC CANCRINITE

The various characteristics of the resulting cancrinite include: Fourier Transform Infrared (FT-IR) spectroscopy, X-ray diffraction, thermal gravimetric analysis and scanning electron microscopy.

#### FOURIER TRANSFORM INFRARED (FT-IR) SPECTROSCOPY

The characterization of the synthesized zeolites cancrinite with transmission Fourier transform infrared spectroscopy (FT-IR) is described Fig. (2). FT-IR spectroscopy is used to probe the structure of the zeolites and monitor reactions in zeolite pores. Specifically, structural information can be obtained from the vibrational frequencies of the

zeolite lattice observed in the range between 200 and  $1500\text{ cm}^{-1}$  (Jentys and Lercher, 2001; Li, 2005). In general, each zeolite has characteristic infrared pattern. However, some common features are observed which, include :internal tetrahedral ( $1250\text{-}920\text{ cm}^{-1}$ , asymmetrical stretch ( $n_{\text{asym}}$ ); ( $720\text{-}650\text{ cm}^{-1}$ , symmetrical stretch ( $n_{\text{sym}}$ ); ( $500\text{-}420\text{ cm}^{-1}$ , T-O bend; external linkages: ( $650\text{-}500\text{ cm}^{-1}$ , double ring vibrations; ( $420\text{-}300\text{ cm}^{-1}$ , pore opening vibrations; ( $1150\text{-}1050\text{ cm}^{-1}$ , asymmetrical stretch; ( $820\text{-}750\text{ cm}^{-1}$ , symmetrical stretch. The FT-IR-spectral data of the synthesized zeolite cancrinite is presented in Table (1). The double rings (D4R and D6R) in the framework structures of the zeolitic ( $500\text{-}650\text{ cm}^{-1}$ ) is near to  $653\text{ (s)}\text{ cm}^{-1}$  which is characteristics cancrinite (Barnes et al., 1999). The bands at  $462\text{ (s)}\text{ cm}^{-1}$  of cancrinite is near the absorption bands within the range  $420\text{-}500\text{ cm}^{-1}$  which are related to the T-O-T bending of vibration mode (T = Al, Si), respectively. These absorption bands characterizing T-O bending vibrations may shifted to lower frequencies due to decreasing Si/Al ratio in the internal linkage due to the different length of the Al-O and Si-O bands (Li, 2005; Mohammed et al, 2013). The bands,  $724\text{ (s)}\text{ cm}^{-1}$  of cancrinite is near the bands in the range  $720\text{-}790\text{ cm}^{-1}$  is associated with symmetric stretching vibration of 4-membered rings. Fig. (2). this band should be assigned to the 4-membered ring vibrations. Because these rings contain the lowest number of members of all rings occurring in the zeolite structure, therefore the bands due to these rings occur at relatively high wave numbers in the pseudo lattice band range. (Sitarz et al., 1997). The

bands (1638) (s)  $\text{cm}^{-1}$  of cancrinite is near the bands at 1647 and 1648  $\text{cm}^{-1}$  (Lewis sites) region is assigned to the zeolitic water in the channels of zeolite (Blanco et al., 1989). The bands at spectra 3446, 3460 and 3482 are attributed to the asymmetric stretching mode of molecular water coordinated to the edges of the zeolite channels (Zhao et al., 2006; Faghihian et al., 2009). The bands 3602 (b)  $\text{cm}^{-1}$  of cancrinite is near the

bands that are attributed to the asymmetric stretching mode of molecular water coordinated to the edges of the zeolite channels (Zhao et al., 2006; Faghihian et al., 2009). And that located at the lowest wave numbers, i.e. at about 466 and 377  $\text{cm}^{-1}$ ; correspond to the characteristic bending vibrations carried out in the 4-membered rings. (Mozgawa et al., 2005) Table (1).

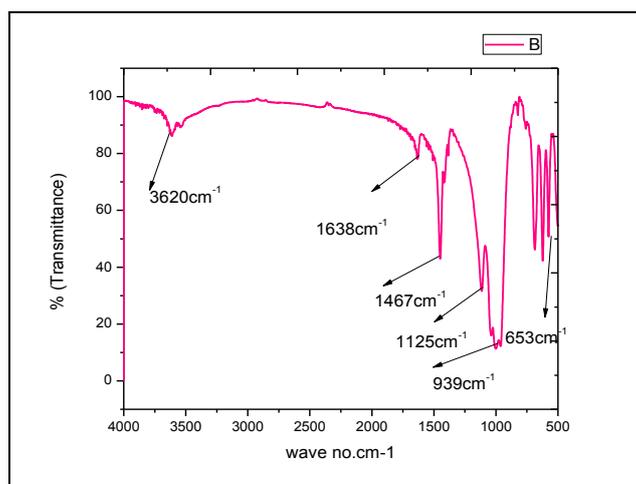


Fig. (2). FT-IR spectrum of cancrinite

Table (1): Fourier Transform Infrared (FT-IR) Spectroscopy of the synthesized cancrinite

Cancrinite	Characteristic band ( $\text{cm}^{-1}$ )	Analysis of bands
	3602 (b)	O—H stretching
(1638) (s)	Bending H—O—H	
1467 (m)	Na-T stretching	
1125 (m)	– vas Si-O(Si) and vas Si-O(Al)	
939 (m)	vs. Si-O-Si	
724 (s)	Bending vs.-O-Al O—T*—O	
653 (s)	O-Si-O	
462 (s)	T-O-T	

### X-RAY DIFFRACTION

The powder XRD pattern shows only reflections resulting from cancrinite and is consistent with the space group P63. The intensity distribution and reflections show that there are no indications of the presence of extraneous phases or amorphous materials. As shown in the XRD

pattern Fig. (3) Cancrinite is the predominant mineral phase in the synthesized sample, which can be identified by its distinctive reflections at  $2\theta = 15.57^\circ$ ,  $25.77^\circ$  and  $35.83^\circ$ , it is near to that reported by (Zhao et al., 2004). Cancrinite is the predominant mineral phase in the synthesized sample, and is identified by its

distinctive reflections at  $2\theta = 14.13^\circ$  and  $24.31^\circ$ .

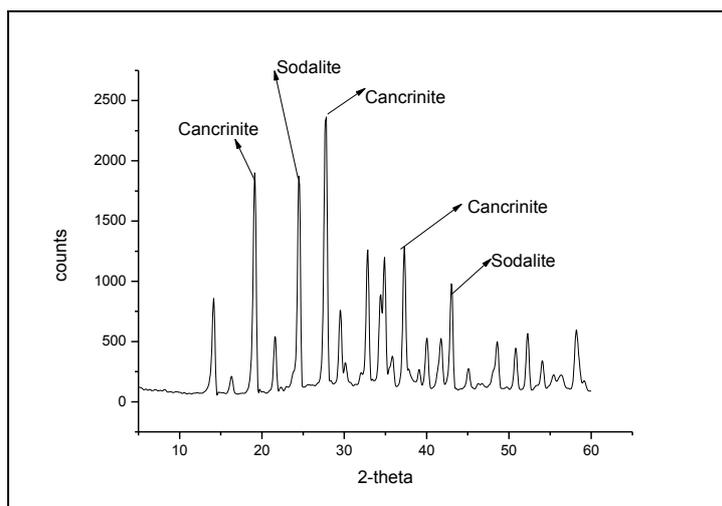


Fig. (3) X-ray diffraction pattern of cancrinite

### SCANNING ELECTRON MICROSCOPE (SEM)

To characterize the morphology of the synthetic zeolite SEM images were investigated. Fig. (4) demonstrated the

occurrence of well crystallized hexagonal and octahedral morphology of the synthetic materials. Cancrinite and sodalite morphology and characteristic was supported by many authors (Porcher et al., 2000; Lapides et al., 2007; Ríos et al., 2009).

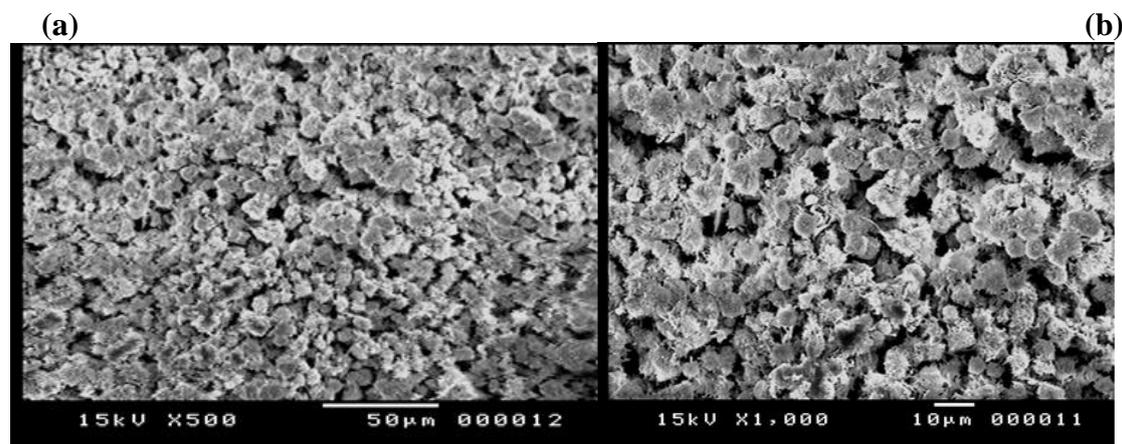


Fig. (4). SEM images of cancrinite.

### THERMAL GRAVIMETRIC ANALYSIS (TGA)

The thermal behavior of synthesized cancrinite was evaluated by TGA and DTG in air at a heating rate of  $10\text{ C}^\circ\text{ min}^{-1}$  are shown in Fig. (5), while Table (2) gives the temperatures for various percentages mass loss. The synthesized product show up to three dehydration steps

(0-8% weight loss). The first step is a fast and ranges between  $27\text{ C}^\circ$  and  $153\text{ C}^\circ$ ; which may be attributed to loss of observed moisture and entrapped solvents. The second step is also fast degradation between  $153$  and  $423\text{ C}^\circ$ . The third step is also fast between  $423\text{ C}^\circ$  and  $600\text{ C}^\circ$ . The positions of these DTG peaks and the number of dehydration steps can be attributed to the different compensating cation-water

binding energies. As well as to the different energy associated with the diffusion of the desorbed water through the porous structure of the synthesized product. Their mass loss percentages reflect the water loss

from the zeolite structure, and the amount of desorbed water is related with the number of compensation cations in the framework of the zeolite (Covarrubias et al., 2006).

Table (2): Thermal analysis of the synthesized cancrinite.

Cancrinite	Temperature (°C) for various percentage decompositions*			
	152	340	380	480

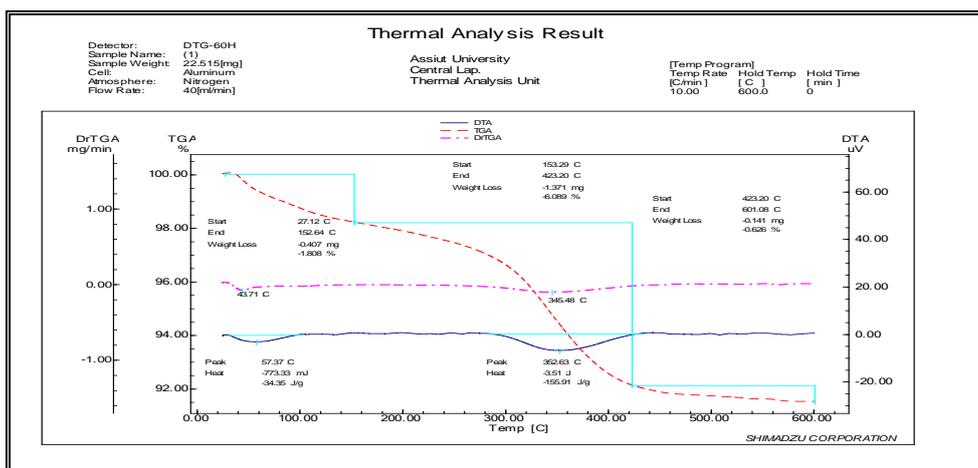


Fig. (5). TGA Thermo gram of cancrinite

#### 4. GROUND WATER TREATMENT NITRATE ADSORPTION EXPERIMENTS

The nitrate adsorption experiments were conducted using contaminated ground water samples from Wadi El Assiuti of known initial concentration. Batch experimental mode was adopted due to its simplicity. In the 1st set of experiments, 1-50 ml of ground water was taken in 100 ml glass beaker.

- 2- A dose of 0.5 g of synthetic cancrinite was added.
- 3- The beaker with contents was placed in a thermostatic shaker operated at 200 r/min
- 4- After 1 h the samples were filtered through a whatman Filter Paper No. 41.

In a second set of experiments, the effects of adsorbent mass, pH, temperature and time on nitrate removal from water were explored by varying the initial solution pH from (6±0.2) to (10±0.5) and time from 1h to 3h. A final set of experiments involved the use of groundwater samples were analyzed for nitrate levels before contacting them with different doses of sorbents. The equilibrium nitrate concentration was then determined.

#### 4.1. RESULTS AND DISCUSSION EFFECT OF ADSORBENT MASS

The number of active sites relates to adsorbent mass and hence sorption performance. The effect of adsorbent mass on the nitrate percentage removal under

room temperature for 1h and at solution pH is shown in Fig. (6). It is clear that an increase in adsorbent mass resulted in an increase in the removal of nitrates from water. Specifically, nitrate removal increases from 60% when the sorbent mass is 0.5 g.(50 ml)/L to 93.5% when the sorbent mass is 1.5 g.(50 ml/1, due to an increase in

available sorption sites. However, it is observed that the increase in nitrate percentage removal is not directly proportional to adsorbent mass. One plausible reason could be due to overlap of active sites at higher adsorbent masses resulting in reduced effective surface area required for sorption.

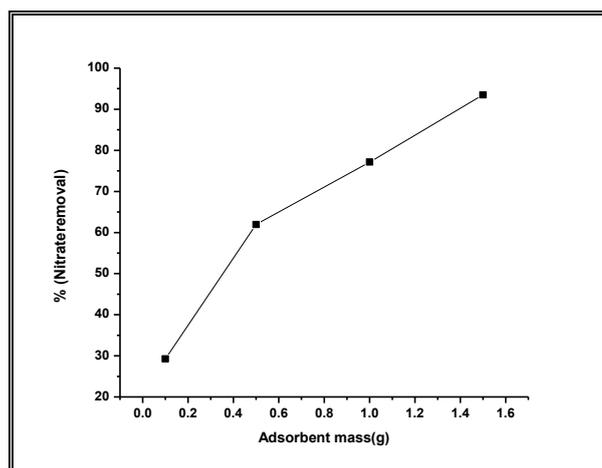


Fig. (6): Effect of adsorbent mass on nitrate removal from ground water sample by cancrinite

## 2. EFFECT OF pH

Solution pH is one of the factors that have been found to significantly affect the sorption process (Onyango et al., 2006). A study was therefore undertaken to ascertain to what extent pH affected the sorption of nitrate. Table (3) summarizes the effects of initial solution pH (6-8.3) on the removal of nitrate at room temperature, 1h and at cancrinite dosage 0.5g. The system (solution–solid) pH at equilibrium is also included. Results reveal that nitrate removal from ground water is marginally affected by water pH. With no electro kinetic data at this stage, it can only be hypothesized that the surface charge on cancrinite was not significantly affected by pH changes. A confirmation is required to ascertain this. The slight increasing in nitrate adsorption with decreasing in pH

from 10.4 to 6 and the highest removal efficiency occurred at pH from (6-7.6). It could be due to interaction during passive transport in the pores and competition between OH- and NO<sub>3</sub>- anions for active sites. One disadvantage of using adsorption processes in removal of anionic contaminants from water inheres in most sorption media's inability to perform adequately at higher pH values. Indeed several researchers have reported a significant reduction in media performance in nitrate removal from water at near neutral and alkaline pH (6.5-8.5), the pH range typical of natural systems such as groundwater (Cengeloglu et al., 2006; Chatterjee et al., 2009; Chatterjee and Woo, 2009). Such as cancrinite used in this study, whose performance does not deteriorate with pH changes is desirable for water

treatment. Meanwhile the pH of the system (solution-solid) after sorption was found to increase when the initial pH was acidic and to decrease when the initial pH was alkaline.

This is due to the buffering effect of the zeolite. Sorbents normally shift solution pHs or their point-of-zero charge (pH pzc). (Onyango, 2006).

Table (3) effect of pH on Nitrate removal from ground water sample by cancrinite

Initial pH	Final pH	Removal (%)
8	10.4	30
8	9.75	62
6	7.6	83
6	6.5	64
6	6-5.8	-8.7

### EFFECT OF TEMPERATURE

The effect of temperature was investigated in a range of 25-45°C at 1h, dosage 0.5g and solution pH is shown in Fig. (7) It was observed that an increase in temperature resulted in a minor decrease in nitrate uptake by cancrinite. This clearly indicates that the adsorption process was exothermic. Similar observations in which adsorption decreased with an increase in temperature were recently reported (Chatterjee and Woo, 2009) for nitrate adsorption by cancrinite. Temperature may or may not have a significant effect on adsorption depending on whether the

process is chemical or physical in nature. When the process is chemical in nature, a higher energy barrier has to be overcome and hence temperature changes result in a significant (either a large increase or large decrease in adsorption) effect on adsorption. Conversely, a minor effect is normally observed when the process is physical in nature. The results of this study therefore reveal further that the nitrate adsorption process is physical in nature, involving coulombic electrostatic forces between the positively-charged of cancrinite surface and negatively-charged nitrate ion.

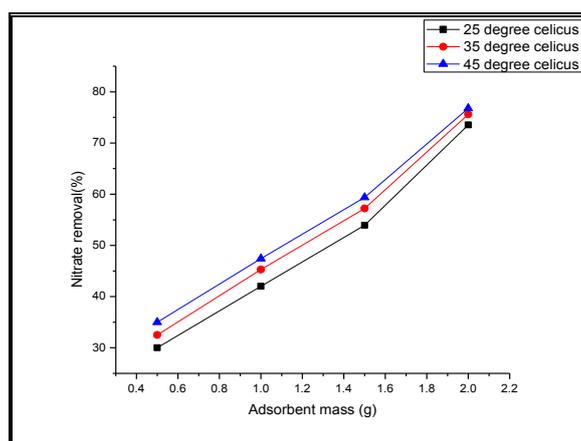


Fig. (7): Effect of temperature on nitrate removal from ground water sample by cancrinite

### EFFECT OF TIME

The amount of adsorptions,  $q_e$ , versus lated times was depicted for different nitrate concentrations and present in the Fig.

represents the effect of contact time on nitrate adsorption for sample. The rate of nitrate adsorption Fig. (8) can be divided into two parts; one represents rapid nitrate

adsorption and another represents slow nitrate adsorption. Duration time for rapid nitrate adsorption was approximately 30 minutes. During this period, the tendency of adsorbent to adsorption was high and therefore, the slope of adsorption curve was steep. Slow adsorption rate was between 30 and 90 minutes. During this period, the

slope of adsorption curve was gradually flattened, and the nitrate adsorption was gradually decreased until reaching zero. This may be occurs as a result of the external surface of cancrinite that is rapidly saturated by nitrate anion and therefore the adsorption rate reduces. (Hamdi et al., 2013).

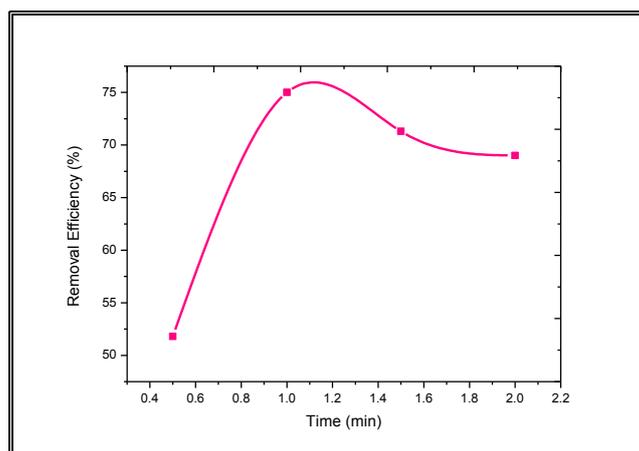


Fig. (8): Effect of time on nitrate removal from ground water sample by cancrinite

#### ADSORPTION ISOTHERM OF $\text{NO}_3^{-1}$ ION BY SYNTHETIC CANCRINITE

Langmuir and Freundlich are the best models to explain the trend of adsorption based on the essence of adsorbents saturated with adsorbate after enough contact time (Qafoku et al., 2000; Hizal and Apak, 2006; Bhatnagar et al., 2010; Hamdi et al., 2013). The study was carried out by contacting 0.5g of the previous synthetic zeolites with different concentrations (17, 42, 74, 94 and 100) ppm from solutions under room temperature, for 1 h and at solution pH on the shaker.

The final concentration of nitrate in solution was determined by measuring the absorbance by spectrophotometer (using kits). The data was fitted into the following isotherms: Langmuir, Freundlich, which are shown in Fig. (9a, b).

Langmuir adsorption isotherm is given as equation (1)

$$q_e = q_{\max} \times C_e \times K / 1 + C_e \times K \quad (1)$$

Where  $q_e$  is the amount of the solute adsorbed per mass unit of adsorbent (mg/g);  $C_e$  is the equilibrium concentration of the aqueous phase (mg/L); and  $q_{\max}$  is the maximum Amount adsorbed.

The parameters,  $q_{\max}$  and  $K$ , are Langmuir constants. And  $q_e$  can be calculated buy equation (2)

$$q_e = (C_i - C_e)V/X \quad (2)$$

where  $q_e$  is the amount of the solute adsorbed per mass unit of adsorbent (mg/g),  $C_i$  is the initial concentration in the aqueous phase (mg/L),  $C_e$  is the concentration in the aqueous phase at equilibrium (mg/L),  $V$  is the volume of the aqueous phase (L), and  $X$  is the weight of the adsorbent (g).

Freundlich isotherm is an empirical equation. The nonlinear form of Freundlich's equation is written as equation (3) (Zheng and Bennett, 2002).

$$qe = KfCe^{1/n} \quad (3)$$

Where  $qe$  is the amount of the solute adsorbed per mass unit of adsorbent (mg/g),  $Ce$  is the equilibrium aqueous pollutant concentration (mg/L),  $Kf$  is Freundlich constant, and  $n$  is Freundlich exponent,  $Kf$  is the indicator of adsorption capacity, and  $1/n$  is a measure of intensity of adsorption.

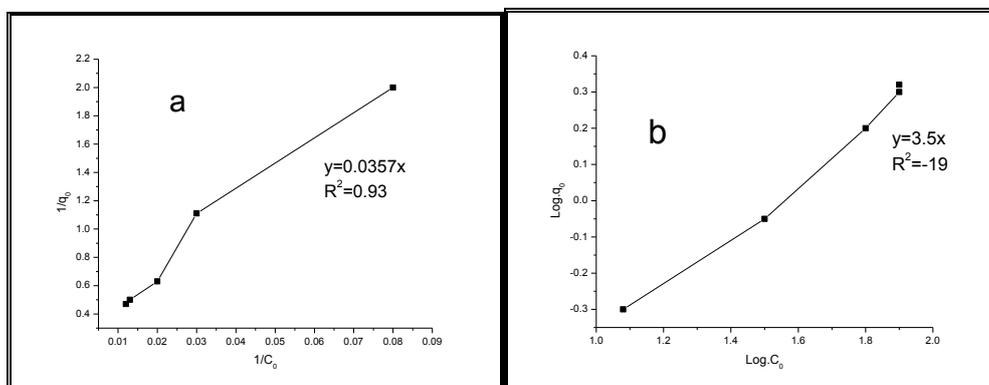
Freundlich is an exponential equation which can be used to determine the values of parameters. The logarithm conversion is one way to determine Freundlich parameters. Therefore converts to  $\log qe = \log Kf + 1/n \log Ce$ . By plotting  $\log qe$  against  $\log Ce$ , the values of Freundlich parameters can be determined. The slope of line is the exponent and the logarithm of intercept is the constant of Freundlich parameters.

**Table (4):** Parameters for plotting Langmuir, Freundlich, and Adsorption Isotherms of nitrate ion by cancrinite

$C_0$ (mgNO <sub>3</sub> <sup>-</sup> /L)	$C_e$ (mgNO <sub>3</sub> <sup>-</sup> /L)	$q_e$ (mg/g)	$1/C_e$	$1/q_e$	Log. $C_e$	Log. $q_e$
17	12	0.5	0.08	2	1.08	-0.3
42	31	0.9	0.03	1.11	1.5	-0.05
74	58	1.6	0.02	0.63	1.8	0.2
94	75	1.9	0.013	0.5	1.9	0.3
100	79	2.1	0.012	0.47	1.9	0.32

**Table (5):**  $R_L$  values for nitrate ion concentrations

Nitrate ion concentration (ppm)	Cancrinite	$R_L$ value
17		0.05
42		0.023
74		0.013
94		0.01
100		0.0099



**Fig. (9)** (a) Langmuir adsorption; (b) Freundlich adsorption isotherm

Based on the data given in Table (4), the plots of  $\log q_e$  versus  $\log C_e$ , and  $1/q_e$  versus  $1/C_e$  were depicted to show the Langmuir and Freundlich isotherms, respectively Fig. (9 a, b). The results showed that Langmuir adsorption isotherm had better matching on data with  $R^2 = 0.93$  than Freundlich adsorption isotherm with  $R^2 = -19$ , that may be not obeyed the Freundlich isotherm. Also the characterization of the Langmuir equation can be explained in terms of the equilibrium parameters ( $R_L$ ) which is a dimensionless constant referred to as separation factor or equilibrium parameter equation (4) (Pandey et al., 2010).

$$R_L = 1 / (1 + K_L C_0) \quad (4)$$

The above parameters describes the nature of the adsorption: irreversible ( $R_L = 0$ ); favorable ( $0 < R_L < 1$ ); linear ( $R_L = 1$ ); unfavorable ( $R_L > 1$ ) (Rozada et al., 2007). From the data calculated in table (5), in the case of nitrate ion are favorable ( $0 < R_L < 1$ ); And From this research work, the maximum monolayer coverage capacity ( $q_0$ ) from Langmuir Isotherm model was determined to be 0.0357 for nitrate ion and  $K_L$  (Langmuir isotherm constant) is 0 for

the same ion. This again confirmed that the Langmuir isotherm was favorable for sorption of nitrate ion onto the synthetic zeolite (cancrinite) under the conditions used in this study (Zhanga et al., 2000; Unlu et al., 2006).

### 5. APPLICATION OF CANCRINITE FOR NITRATE ADSORPTION FROM GROUNDWATER SAMPLES IN THE STUDY AREA.

The synthetic cancrinite was applied in the removal of *nitrate* ions from ground water samples from Wadi EL-Assiuti. The sorption studies were carried out at solution pH, time 1h and cancrinite dosage 0.5g. The results are shown in Table (5).

The results clearly show that the synthesis cancrinite has good adsorption capacity for nitrates. Because cancrinite and sodalite prefer nitrate groups to hydroxide groups in their cages or channels under the conditions used. This observation concurs well with those of previous researchers (Buhland Loens, 1996; Hongting et al., 2004). According to the results in Table (6) all the 13 samples show that cancrinite can be used for nitrate removal.

**Table (6):** Application of cancrinite for nitrate removal from groundwater samples in the study area.

No. of sample	NO <sub>3</sub> <sup>1-</sup> (ppm)		Removal efficiency, %
	Before adding cancrinite	After mixing with cancrinite	
1	42	31	27
2	17	12	30
3	28	22	22
4	80	65	19
5	41	33	8
6	94	75	21
7	74	58	22
8	100	79	21
9	100	79	21
10	92	73	21
11	79	63	20
12	72	57	21
13	21	16	24

## 6. CONCLUSIONS

In this article, we could successfully use cancrinite for nitrate removal from groundwater. The first stage of experiments was carried to Batch experimental tests for the ability of cancrinite for nitrate removal from groundwater at initial nitrate concentrations 92 ppm, initial pH values (6.1–8.3), at time 1h and under normal temperature. It is exhibited the highest nitrate removal efficiency was about 83% at pH 7.6, and initial nitrate concentration of 92mg/L NO<sub>3</sub><sup>-</sup>.

The second stage of experiments was carried to application of cancrinite to nitrate removal from groundwater and the results show that cancrinite can be applied as an adsorption system to remove nitrates present in ground water. And it exhibited the highest nitrate removal efficiency about 30% at pH values of the ground water samples of the studied area (8.1–9.75), and various initial nitrate concentrations (17 to 41, 72 to 80 and 92 to 100) mg/L, at time 1h under normal temperature.

The Langmuir constants model for NO<sub>3</sub><sup>-</sup> ion sorption on the adsorption isotherms is fitted well. The R<sub>L</sub> value in the present investigation was equal or less than one, indicating that the adsorption of NO<sub>3</sub><sup>-</sup> ion by cancrinite is favorable.

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## توليف، مواصفات وتطبيقات الكانكرينيت في معالجة المياه الجوفية بمنطقة

### وادي الأسيوطي - أسيوط - مصر

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### الملخص العربي :

يعتبر الكانكرينيت من أكثر الأنواع النادرة من مجموعة فيلدسباتويد، وتصنف أيضا على أنها من معادن الزيولايت، نظرا لهيكلها المسامي المفتوح، والذي يعطي خصائص المنخل الجزيئي. وقد تم تخليقها بنجاح بالطريقة الحرارية المائية في غياب القالب العضوي عند ١٨٠ درجة مئوية لمدة ٥ أيام بعد التقليل بسرعة عالية والتوليف في تحضير الخليط طبقا للتركيب المولاري  $\text{Na}_2\text{O} : 6\text{SiO}_2 : 1.6\text{Al}_2\text{O}_3 : 9\text{H}_2\text{O}$ . وقد تمت دراسة خصائص المادة المخلفة بواسطة حيود الأشعة السينية (XRD) والميكروسكوب الإلكتروني (SEM) والتحليل الطيفي للأشعة تحت الحمراء (FT-IR) و الخواص الحرارية التحليل الوزني الحراري (TGA). و ايضا تم اختبار الكانكرينيت كمادة مازة لازالة أيونات النترات من عينات المياه الجوفية. وقد تم تقييم كفاءة الكانكرينيت للامتزاز من ايونات النترات باستخدام تركيزات مختلفة من كل عينات المياه ، في درجة حرارة الغرفة. مع الاحتفاظ بجميع العوامل الأخرى (درجة الحموضة (ph) والزمن ) ثابتة فيما يتعلق بالتركيز الابتدائي من أيونات النترات في عينات المياه. وقد وجد ان الكانكرينيت لديه كفاءة إزالة جيدة لأيونات النترات عند درجة حموضة (ph) ٦-٧.٦، جرعة ١٠ غرام / لتر من المادة المازة ، زمن ٦٠ دقيقة كما تم تطبيق عدة نماذج لإزالة أيونات (النترات) باستخدام (الكانكرينيت ) المخلوق ومن هذه النماذج منحنيات (Langmuir ,Freundlich isotherm's ) وكانت النتائج مناسبة و ( $R_L > ٠$ )، مشيرا إلى أن امتزاز هذه الملوثات على الكانكرينيت تتم بصورة جيدة .

**كلمات البحث:** كانكرينيت، المياه الجوفية، توصيف، محتويات العنصر، معالجة المياه.