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## PRE-TREATMENT OF DESALINATION FEED SEAWATER BY JORDANIAN TRIPOLI, POZZOLANA AND FELDSPAR: BATCH EXPERIMENTS

*In this research, composites of layered double hydroxide (LDH) with three Jordanian natural raw materials: Tripoli (T), Pozzolana (P) and Feldspar (F) were prepared by co-precipitation and have been used for feed seawater pre-treatment. The data reveals that percent adsorption decreased with increase in initial concentration, but the actual amount of adsorbed ions per unit mass of LDH/T-P-F increased with increase in metal ion concentrations. The values of  $\Delta G$  were negative and within 21 to 26 kJ/mol, while the values of  $\Delta S$  were positive, with  $\Delta H$  within the range of 0.1 to 25 kJ/mol. The values of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  indicate the favorability of physisorption and show that the LDH/T-P-F composites have a considerable potential as adsorbents for the removal of ions from seawater.*

*Key words: pre-treatment; feed seawater; ceramic filters; Tripoli; Pozzolana; Feldspar.*

Pre-treatment of the feed water entering a desalination unit such as MSF involves reduction of salinity and hence reducing or in some cases eliminating scale forming species (in MSF or MED for example) to a certain extent. This will increase the efficiency of the process, reduce the pumping power (in RO systems), reduce or eliminate the scale and consequently reduce the cost. Using low-cost materials for pre-treatment is increasing world-wide because of its positive impact on the net production cost. Various treatment techniques and processes have been used to remove the pollutants from contaminated water. Among all the approaches proposed, adsorption is one of the most popular methods and is currently considered as an effective, efficient, and economic method for water purification. The adsorbents used include activated carbon, clay minerals, zeolites, metal oxides, agricultural wastes, biomass and polymeric materials [1]. In this research, three Jordanian low-cost natural raw materials (Tripoli, Pozzolana and Feldspar "T-P-F") have been chosen for seawater

pre-treatment. The selected adsorbents were used because they are available in huge amounts in Jordan, low-cost, environmentally friendly and have high adsorption capacity [2].

Tripoli, from south Jordan (Tafila area), is amorphous, white, soft and highly porous beds of quartz (silica-opal-A) [3]. Tripoli is a clay mineral, contains more than 92% SiO<sub>2</sub>, available in large quantities in the southern part of Jordan [4]. Al-Zaydien [5] studied the adsorption of methylene blue from aqueous solution onto a low-cost natural Jordanian Tripoli. The results show that the natural Jordanian Tripoli, abundant low-cost clay, can be used as sorbent for the removal of methylene blue dye from aqueous solutions.

Pozzolana, from south Jordan (Jabal Al Ataita), is a natural volcanic slag, covered a large area in Jordan. Many researchers studied the using of pozzolana and volcanic tuff in water and wastewater treatment. Attili [6] has evaluated the Jordanian phillipsitic tuff for applications in water softening, removal of ammonium and toxic heavy metal ions in laboratory and pilot plant scale. Ed-Deen [7] has evaluated zeolites from Tell Rimah for industrial wastewater treatment. The results have indicated that Tell Rimah zeolitic tuff showed high selectivity for the removal of Cu, Cr, Ni and Zn from electroplating factory effluents and could be used for removing Pb and Fe from the wastewater

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of the Battery Factory. Al Dwairi [8,9] studied the characterization of Jordanian basaltic rocks and zeolitic tuff and the potential use of zeolitic tuff in removing Zn and Pb from domestic wastewater. Ibrahim and Jbara [10] have used natural phillipsite-faujasite tuff from Jordan to remove paraquat from synthetic wastewater.

Feldspar is the most abundant mineral group in the world, forming around 60% of the earth's crust, and is found in igneous, metamorphic and sedimentary deposits in most countries [11]. Feldspars occur in high quantities in many locations of Wadi Araba, southern Jordan (where the igneous and metamorphic rocks occurred). They are divided into two major divisions: *i)* potash feldspars and *ii)* soda-lime feldspars. Feldspar minerals are thermodynamically unstable in the near-surface environment and their surfaces are well known to react readily with aqueous solutions, leading to incongruent dissolution at low pH values, but congruent dissolution at neutral and high pH values. Interactions with mineral surfaces are an important control on the environmental transport of trace elements and detrital feldspars are abundant in soils and sediments. However, the interactions of metal ions in solution with the reacting feldspar surface have not been widely explored. The reactions of the feldspar surface with metal ions of Pb(II), U(VI) and Np(V) has been studied [12], and of U(VI) has been studied by Torstenfelt *et al.* [13] and Walter *et al.* [14]. The presence of  $\text{CO}_3^{2-}$  in solution enhances U(VI) solubility at high pH so that sorption usually reaches a maximum at near-neutral pH. Uptake mechanisms differ in detail, depending on pH [15]. This is the first time that feldspar has been used in seawater treatment in Jordan. There is much less information available on sorption of ions by feldspar in Jordan.

Hydrotalcite-like (HT) or layered double hydroxides (LDHs) compounds are a class of synthetic anionic layered clays which can be represented by the general formula  $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{x+}(\text{A}^n)_{x/n}m\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are divalent and trivalent cations in the octahedral sites within the hydroxide layers,  $x$  is equal to the ratio of  $\text{M}^{3+}/(\text{M}^{2+}+\text{M}^{3+})$  with a value varying in the range of 0.17-0.50, and  $\text{A}^n$  is the exchange interlayer anion [16]. Carbonates are the interlayer anions in naturally occurring hydrotalcite. The thermal decomposition of LDH leads to mixed metal oxides, which are characterized by high specific surface areas, homogeneous dispersion of metals. It was found that many kinds of cations, whose ionic radii are not too different from that of  $\text{Mg}^{2+}$ , may be introduced inside the brucite-like sheet, and thus, HT with various com-

positions and structure were obtained. This feature resulted in the occurrence of more synthetic HT compounds, which consequently exploited their further application in various scopes. Wherein, the use of HT as a kind of adsorbent in the water treatment was focused by many researchers. See [1] for details.

## EXPERIMENTAL

### Materials

Tripoli occurs in the silicified limestone unit of the upper cretaceous in Jordan. The formation of Tripoli in Jordan occurs by two mechanisms: tripolization of chert and tripolization of limestone in a substitutional process, controlled by pH fluctuations, when silica-rich solutions replaced the limestone beds, and silica was derived from the dissolution of chert beds as a result of high pH (due to dissolution of Portlandite which occurs in the bituminous limestone). The chemical composition of the natural Tripoli obtained by X-ray fluorescence (XRF) is 93.5%  $\text{SiO}_2$ , 2.39%  $\text{Al}_2\text{O}_3$ , 0.1%  $\text{Na}_2\text{O}$ , 0.08%  $\text{Fe}_2\text{O}_3$ , 0.07%  $\text{CaO}$ , 0.08%  $\text{K}_2\text{O}$  and 0.08%  $\text{MgO}$ . The major peak that appears in the XRD spectra for the natural Tripoli that appears at  $2\theta$  of 26.7 is characteristic of  $\text{SiO}_2$ . Some of the other peaks that appear at  $2\theta$  of 36.5, 39.4, 45.86, 50.3 and 59.9 are also characteristic of quartz and other silicon oxide containing phases [5].

Pozzolana/zeolitic tuff is extracted from Al Ataita volcano south of Tafila. The chemical compositions and the physical properties of pozzolana used in this work are resumed in Table 1. Particle diameters are widely distributed from 4 to 5 mm. Jabal Al Ataita is covered by volcanic rocks, mainly Pozzolana of brown and gray color (tuff) with thickness more than 50 m. It is Tertiary to Pleistocene in age (Bender). The area belongs to the Dana horst which occurs between E-W trending Dana fault in the north and Salawan Fault in the south. Other Faults occur in the area with mainly N-S directions. Lithologically, Jabal Al Ataita recognized three horizons (types) of Pozzolana from the top to the bottom as follows: *i)* brown-dark brown, partly yellow brown (7-15.5 m), *ii)* gray-dark gray, greenish gray, light gray (8-32 m) and *iii)* pale brown, partly gray (7-15 m). The specific gravity reflects the high porosity of the deposit in form of vesicles which is very characteristic of Pozzolana. The specific gravity for the brown type is 1.84 while for the gray-dark gray type is 1.64. XRD analysis of pozzolana/zeolitic tuff samples revealed that most samples are composed of phillipsite as major constituents followed by chapazite and faujasite. Each one has own specific

Table 1. The chemical analysis of Pozzolana

Sample no.	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>
1	10.29	40.87	12.34	13.90	8.58	0.76	1.33	0.04
2	10.99	40.52	12.62	13.42	8.38	0.65	2.41	0.06
3	12.31	44.21	16.47	13.73	6.84	0.55	2.93	0.09
4	13.12	40.27	13.63	12.28	8.95	1.31	2.59	0.10
5	12.85	42.88	14.97	13.14	7.04	0.68	2.58	0.12

gravity and due to that phillipsite, chapazite and faujasite can be separated from each other [17].

All the feldspars have similar physical properties; the samples used in this study are pink, vitreous, and tubular with hardness of about 6. Potash feldspars are found in acid igneous rocks such as granite, pegmatite and syenite. They occur associated with quartz and micas. The plagioclase feldspars are found in the basic igneous rocks. They are found associated with hornblende, augite or olivine. Both types of feldspars are also found in metamorphic rocks. The feldspar structure, similar to the structure of the various polymorphs of SiO<sub>2</sub>, consists of an infinite network of SiO<sub>4</sub> as well as AlO<sub>4</sub> tetrahedral. The feldspar structure can be considered a derivation of the SiO<sub>2</sub> structures, by incorporation of Al into the tetrahedral network, and concomitant housing of Na<sup>+</sup>, K<sup>+</sup> or Ca<sup>2+</sup> in available voids. When only one Si<sup>4+</sup> (per feldspar formula unit) is substituted by Al<sup>3+</sup>, the structure can be neutralized by incorporation of one K<sup>+</sup> or one Na<sup>+</sup>. Similarly when two Si<sup>4+</sup> (per feldspar formula unit) are substituted for by Al<sup>3+</sup>, the electrostatic charge of the network can be balanced by a divalent cation such as Ca<sup>2+</sup>. Feldspars occur in high quantities in many locations of Wadi Araba, southern Jordan (where the igneous and metamorphic rocks occurred). Table 2 shows the main major oxides of feldspar in many localities of Wadi Araba. A mineralogical study was performed by Natural Resources Authority - Jordan, on representative samples from Wadi Al-Jaishieh feldspar deposit; the main essential minerals were found to be orthoclase, plagioclase, microcline and quartz [18].

## Methods of preparation and analysis

### Preparation of the LDH-natural material composite

The Mg<sup>2+</sup>/Al<sup>3+</sup>(NO<sub>3</sub><sup>-</sup>) hydrotalcite (HT) with an Mg/Al ratio of 3:1 was prepared from their nitrate salts. Magnesium nitrate hexahydrate (30.8 g, 0.12 mol) and aluminum nitrate nonahydrate (15.0 g, 0.04 mol) were dissolved in 100 ml of deionized and de-carbonated water. The pH of the solution was adjusted to ≈10 by addition of NaOH (2 M). Accurately weighed 15 g of natural material (Tripoli, Pozzolana or Feldspar) were added to the mixture by ratio (3:1) for co-precipitation. The slurry was stirred for 2 h at room temperature under nitrogen atmosphere and then filtered, washed thoroughly and dried under vacuum at 80 °C. After drying the product was grinded for the adsorption experiments, filter preparation or filter casting and sintering in the second step. X-ray diffraction pattern of the synthetic hydrotalcite has shown that, before calcination, the hydrotalcite clearly has a layered structure. The most intense peak of the hydrotalcite is actually 3 peaks very close together. This gives a d(001) spacing of 7.81-7.61Å, which corresponds to the distance between the hydroxyl layers. Similarly, three peaks at 3.92-3.81Å were present, which is attributed to the d(002) peak. The three d(001) and d(002) peaks potentially indicate the presence of hydrotalcites with three interlayer spacings. A possible explanation is there are three different arrangements of the anion between the layers, such as the anion laying flat on the surface, perpendicular to the surface, or somewhere in between [19].

### Batch seawater pre-treatment experiments

The adsorption experiments were conducted by using a certain amount of the material (T-P-F) “a

Table 2. Major oxides of feldspar of Wadi Araba

Sample no.	SiO <sub>2</sub>	K <sub>2</sub> O	TiO <sub>2</sub>	Na <sub>2</sub> O	MgO	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
1	73.70	2.60	0.20	3.70	0.40	1.60	1.60	13.14
2	64.10	10.99	0.01	2.05	0.00	0.11	0.19	18.67
3	74.25	6.83	0.26	1.58	0.01	0.81	1.49	13.44
4	75.52	5.83	0.03	2.44	0.20	0.50	0.24	13.00
5	77.01	6.06	0.01	1.48	0.01	0.38	1.38	12.95

batch system" (2 g in 100 ml beaker), 50 ml of filtered seawater are added and the beaker kept in thermostated conditions at the desired temperature, viz., 30, 40, 50 and 60 °C, with continuous shaking for 2 h. Natural seawater samples were taken from the Gulf of Aqaba. Batch mode was selected because of its simplicity and reliability. The samples are then filtered and kept in polyethylene bottles for chemical analysis. The water samples were analyzed using ion chromatography (IC) (Dionex-100 with an AG4A-SC guard column, AS4SC separating column, an SSR1 anion self-regenerating suppressor and a conductivity meter). All experiments were performed in duplicate at least and mean values were presented with a maximum deviation of 3%.

**RESULTS AND DISCUSSIONS**

The removal of ions from different concentrations of seawater samples (100, 75, 50, 25 and 10%) in the batch mode are drawn for the removal of Ca<sup>2+</sup>, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> by Tripoli, Pozzolana and Feldspar in Figure 1. They are also shown in Table 3 and drawn for Na<sup>+</sup> and Cl<sup>-</sup> in Figure 2A, for Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> in Figure 2B, and for K<sup>+</sup>, Ca<sup>2+</sup>, F<sup>-</sup>, Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup> in Figure 2C. They are drawn separately because of the large differences in the concentration scale. Natural seawater samples were taken from the Gulf of Aqaba. The results of composite LDH-Tripoli samples are shown here as representative results. Similar trends were found in the pozzolana and feldspar trials.

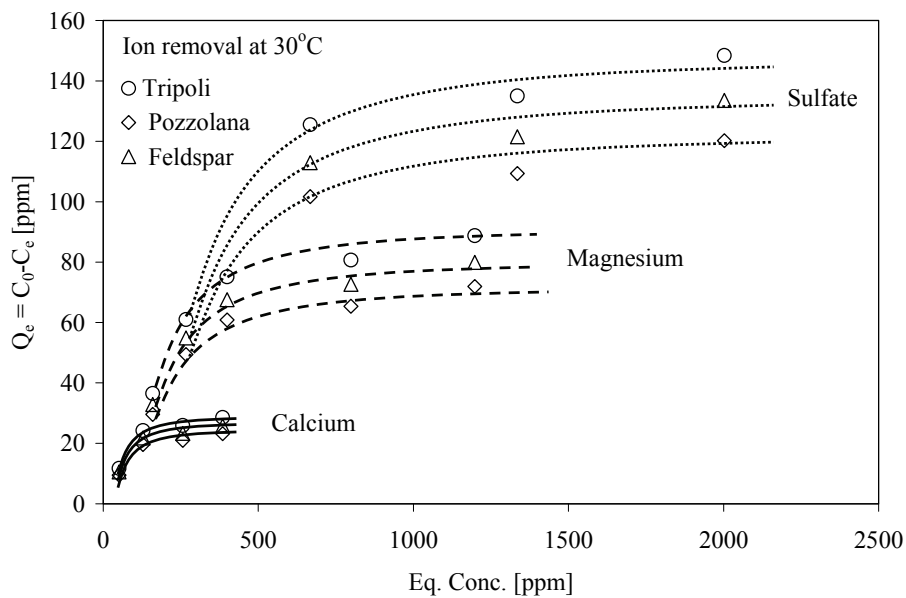


Figure 1. Removal of scale-forming ions, Ca<sup>2+</sup>, Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> by Tripoli, Pozzolana and Feldspar.

Table 3. LDH-Tripoli; removal of ions at different ions' concentrations (100, 75, 50, 25 and 10% seawater)

Species	Initial concentration (seawater original concentration), ppm	Concentration from initial concentration, %			
		75	50	25	10
pH	8.1	8.0	7.9	7.9	7.8
Na <sup>+</sup>	13728	762.9	694.0	645.1	313.6
K <sup>+</sup>	366.8	20.4	18.5	17.2	8.4
Mg <sup>2+</sup>	1597	88.8	80.7	75.1	36.5
Ca <sup>2+</sup>	513	28.6	25.9	24.2	11.7
F <sup>-</sup>	78.8	4.4	4.0	3.7	1.8
Cl <sup>-</sup>	21099	1172.5	1066.6	991.5	481.9
Br <sup>-</sup>	219.1	12.2	11.1	10.3	5.0
NO <sub>3</sub> <sup>-</sup>	197.2	11.0	10.0	9.3	4.5
PO <sub>4</sub> <sup>2-</sup>	-	-	-	-	-
SO <sub>4</sub> <sup>2-</sup>	2669.8	148.4	135.0	125.5	61.0
TDS	40468.7	2248.9	2045.8	1901.7	924.4

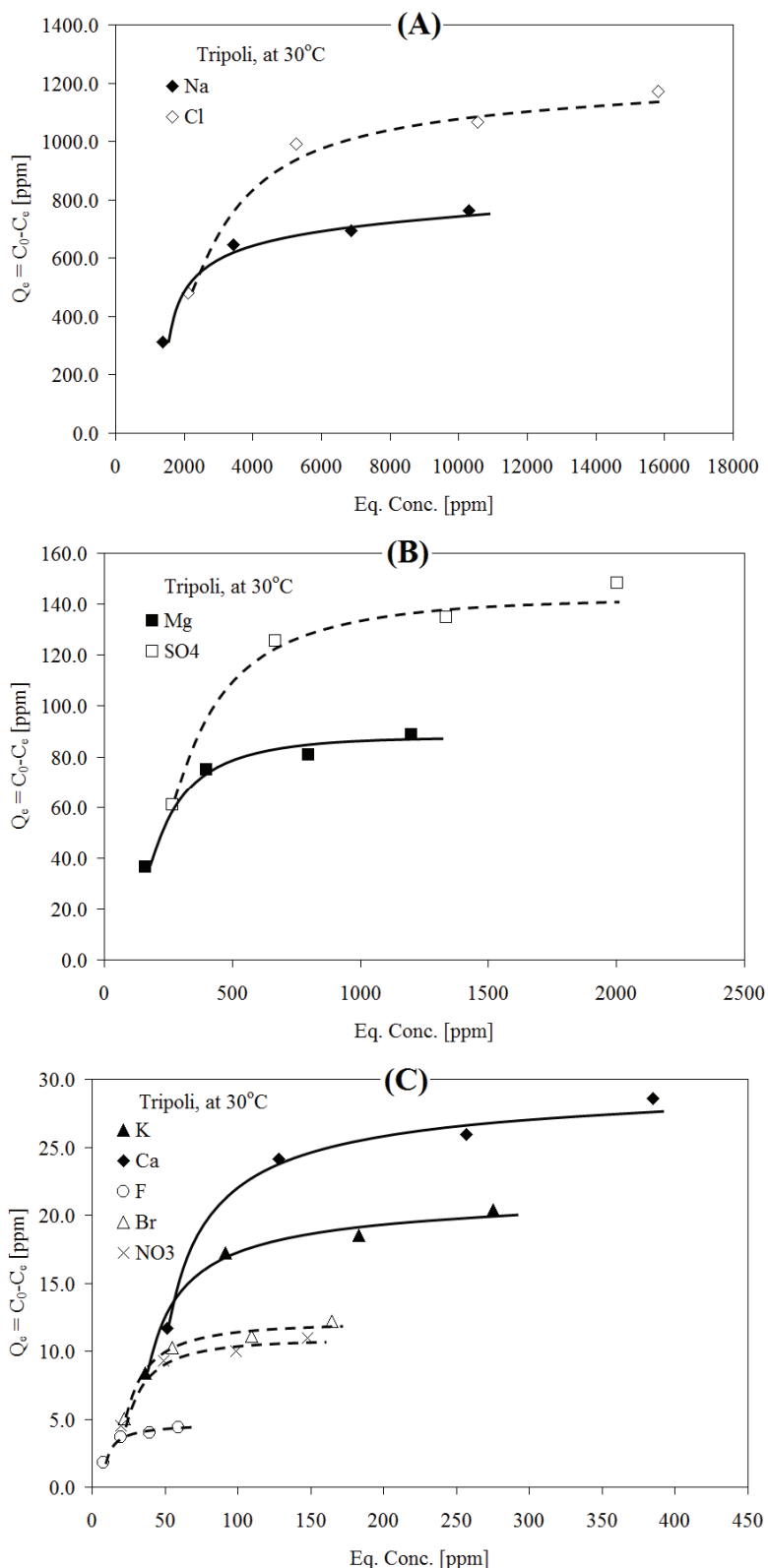


Figure 2. LDH-Tripoli; removal of: A)  $Na^+$  and  $Cl^-$ , B)  $Mg^{2+}$  and  $SO_4^{2-}$  and C)  $K^+$ ,  $Ca^{2+}$ ,  $F^-$ ,  $Br^-$  and  $NO_3^-$ .

The data reveals that percent adsorption decreased with increase in initial concentration, but the actual amount of adsorbed ions per unit mass of

LDH/T-P-F increased with increase in metal ion concentrations. This means that the adsorption is highly dependent on the initial concentration of ions. This is

because at lower concentration, the ratio of the initial number of ions to the available surface area is low; subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer, and hence the percentage removal of the ions is dependent upon initial concentration [20]. The LDH/T-P-F composites could be used for the removal of ions from seawater and it is expected to have a great potential, if it is prepared in a suitable way, to be applied in pre-treatment process, since the results presented here are a single batch experiment. Upon dilution, the percentage removal may reach 25% in a single batch experiment. A multi-pass setup may increase the ions removal to a higher extent, suitable for pretreatment requirements of 80 to 90%. The scaling potential will be calculated and experimentally investigated for a thermal and/or a membrane system.

Adsorption/catalytic reduction process has been found to be efficiently used in water purification. In the recent years, many kinds of adsorbents with the catalytic reduction function were developed and used in removing nitrate, heavy metals, and organic pollutants from water. The modified hydrotalcite-type (HT) adsorbent was used here because it is a typical, low-cost, and easy to prepare adsorbent. As reported, many kinds of ions may enter the interlayer space of HT and consequently be adsorbed. Especially, after calcinations, the reconstruction of the original hydrotalcite with the positive charge layers was obtained [1].

It was found [21] that the co-existing anions in solution lead to the decrease of deionization capacity of LDH for  $F^-$  in the order of  $PO_4^{3-} > SO_4^{2-} > Cl^-$ . The phosphate ions have maximal effect on fluoride removal, and hence other monovalent ions, by LDH. The effect of these anions towards defluoridation may be due to their affinity towards LDH. LDH have greater affinities for anions with higher charge density, *i.e.*, multicharged anions get adsorbed more easily than that monovalent anions. This, indeed, is helping in two aspects; the removal of multivalent ions is the key issue of preventing scale formation in the desalination process, and the low concentration of the multivalent ions in seawater give better chance to remove more monovalent ions and increase the efficiency of the pre-treatment process.

Basic assumption of the Langmuir isotherm is that adsorption takes place at specific homogeneous sites within the adsorbent. The Langmuir isotherm can be represented as [22]:

$$Q_e = \frac{K_L a_L c_e}{1 + a_L c_e} \quad (1)$$

where  $c_e$  is the equilibrium concentration (mg/l),  $Q_e$  is the amount adsorbed at equilibrium (mg/g), and  $K_L$  and  $a_L$  are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The theoretical maximum monolayer adsorption capacity,  $Q_m$  (mg/g), is given by  $K_L/a_L$ .

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor,  $R_L$ , which is defined as:

$$R_L = \frac{1}{1 + a_L c_0} \quad (2)$$

The linear plots of  $c_e/Q_e$  versus  $c_e$  suggest the applicability of the Langmuir isotherm (Figure 3). The value of adsorption efficiency  $Q_m$  and adsorption energy  $b$  of the LDH/T-P-F increases upon increasing the temperature. It can be concluded that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface [20]. The adsorbent prefers to bind to acidic ions and that speciation predominates on the sorbent characteristics, when ion exchange is the predominant mechanism. Further, this confirms the endothermic nature of the processes involved in the system. The separation factor ( $R_L$ ) has been found to be between 0 and 1 which confirms the favorability of the adsorption process [23].

The adsorption capacity of the LDH/T-P-F composite increased with increasing the temperature of the system from 30-60 °C. Thermodynamic parameters such as change in free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) were calculated from the variation of the thermodynamic equilibrium constant  $K$  with the change in temperature.

Gibbs free energy can be calculated from the thermodynamic equilibrium constant,  $K$ , which is defined as follows:

$$K = \frac{a_s}{a_e} = \frac{v_s Q_e}{v_e c_e} \quad (3)$$

where  $a_s$  is the activity of adsorbed ion,  $a_e$  is the activity of the ion in solution at equilibrium,  $v_s$  is the activity coefficient of the adsorbed ion and  $v_e$  is the activity coefficient of the ion in solution at equilibrium. As the ion concentration in the solution decreases and approaches zero, the activity coefficient  $v$  approaches to unity. The last equation may be written as:

$$\lim_{c_e \rightarrow 0} \frac{a_s}{a_e} = \frac{Q_e}{c_e} = K \quad (4)$$

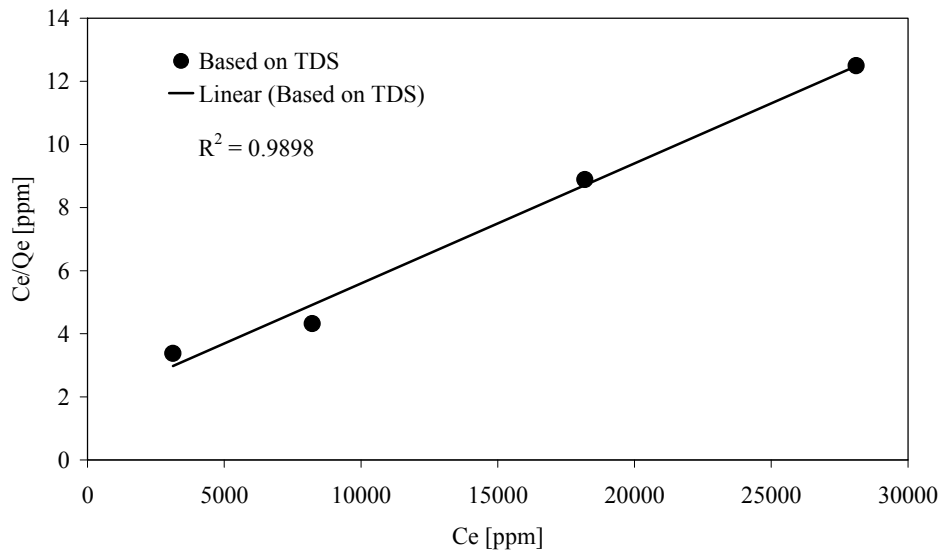


Figure 3. Langmuir linear plot based on TDS values of LDH-Tripoli.

$K$  can be obtained by plotting a straight line of  $\ln (Q_e/c_e)$  versus  $Q_e$  and extrapolating  $Q_e$  to zero. Its intercept gives the values of  $K$  [23].

The adsorption free energy change ( $\Delta G$ ) can be calculated according to:

$$\Delta G = -RT \ln K \tag{5}$$

where  $R$  is the universal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $T$  is the thermodynamic temperature.

Enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) were calculated using the following equation:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{6}$$

where  $K$  is the equilibrium constant,  $T$  is the temperature in Kelvin, and  $R$  is the gas constant. Figure 4 shows the plot of  $-\log K$  versus  $1000/T$ , based on average TDS values, of the three LDH/T-P-F materials.

The  $\Delta H$  and  $\Delta S$  values obtained from the slope and intercept of the Van't Hoff plots have been presented in Table 4. The  $\Delta H$  values are within the range of 0.1 to 25 kJ/mol indicating the favorability of physisorption. The positive values of  $\Delta H$  show the endothermic nature of adsorption and it governs the possibility of physical adsorption. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of the ions adsorption increases, this rules out the possibility of chemisorp-

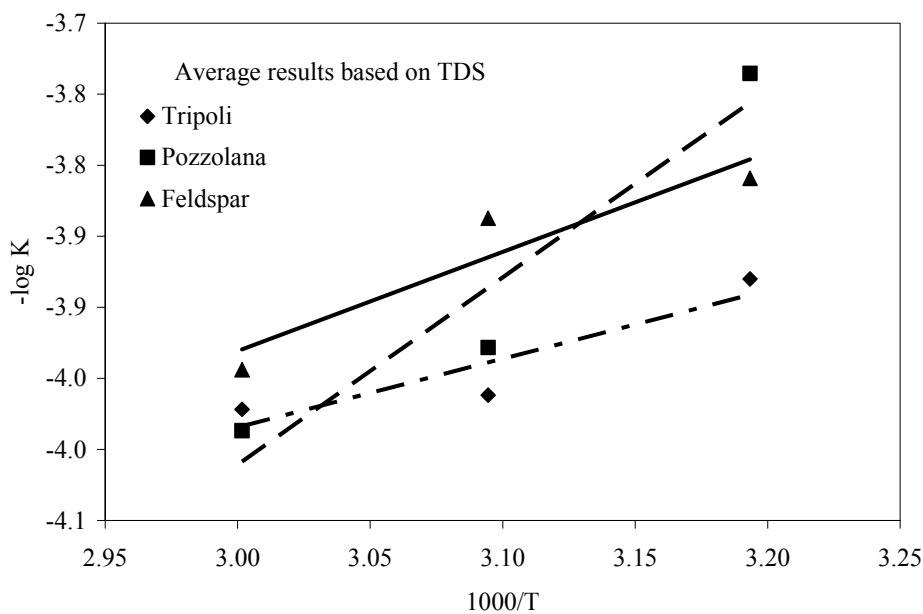


Figure 4. A plot of  $-\log K$  versus  $1000/T$ , based on average TDS values, of the three LDH/T-P-F materials.

Table 4. Average thermodynamics parameters, based on TDS, of ion removal by LDH/Jordan Tripoli, Pozzolana and Feldspar composite

Material	T/ °C	K/ mol L <sup>-1</sup>	ΔG/ kJ mol <sup>-1</sup>	ΔH/ kJ mol <sup>-1</sup>	ΔS/ J mol <sup>-1</sup> K <sup>-1</sup>
Tripoli	30	6923.3	-22.3	9.2	104.0
	40	7782.9	-23.3	-	-
	50	8686.1	-24.4	-	-
	60	9630.4	-25.4	-	-
Pozzolana	30	4140.7	-21.0	25.2	152.5
	40	5700.2	-22.5	-	-
	50	7693.4	-24.0	-	-
	60	10198.2	-25.6	-	-
Feldspar	30	5275.4	-21.6	13.4	115.4
	40	6249.2	-22.8	-	-
	50	7325.6	-23.9	-	-
	60	8505.8	-25.1	-	-

tion. However, lower values of  $\Delta H$  suggest that the ions are physisorbed onto the adsorbent [24]. The negative values of  $\Delta G$  show that adsorption is highly favorable for the ions. However, it also indicates that the ions adsorption were spontaneous. The positive values of  $\Delta S$  show the increased disorder and randomness at the solid solution interface with the adsorbent. During the adsorption there are some structural changes in the ions and the adsorbent. The adsorbed water molecules, which have been displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system. From the results, we could make out that physisorption is more efficient. Enhancement of the adsorption capacity of the LDH/T-P-F composite at higher temperatures has been attributed to the enlargement of pore size and activation of the adsorbent surface [20]. Calcined MgAl-CO<sub>3</sub> layered double hydroxides were used to remove fluoride with the reconstruction of their original layered structure in the presence of appropriate anions [21]. The values of  $\Delta G$  at 30, 40, 50 and 60 °C were -17.18, -17.55, -17.60 and -17.76 kJ/mol, indicating the spontaneous nature of defluoridation, are consistent with our results.

## CONCLUSION

The experimental data correlated reasonably well by the Langmuir adsorption isotherm. The dimensionless separation factor ( $R_L$ ) showed that the LDH/T-P-F composites could be used for the removal of ions from seawater and it is expected to have a great potential, if it is prepared in a suitable way, to be applied in pre-treatment process, since the results presented here are a single batch experiment. Upon dilu-

tion, the percentage removal may reach 25% in a single batch experiment. A positive value of  $\Delta H$  indicated that the adsorption of ions from seawater on LDH/T-P-F composite was endothermic. Since  $\Delta G$  were negative and were accompanied by positive  $\Delta S$ , the reactions were spontaneous with high affinity for ions.

In a next phase project, a pilot plant setup will be developed to ensure a multi-pass process to increase the ions removal; the scaling potential will be calculated and experimentally investigated for a thermal and/or a membrane system.

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NAUČNI RAD

## PREDRETMAN MORSKE VODE KOMPOZITIMA NA BAZI PRIRODNIH SIROVINA IZ JORDANA (TRIPOLI, POZZOLANA I FELDSPAR) U CILJU DESALINACIJE: ŠARŽNI EKSPERIMENTI

*U ovom istraživanju koprecipitacijom su pripremljeni kompoziti sa dvostrukim slojem hidroksida (LDH) od tri prirodne sirovine poreklom iz Jordana: Tripoli (T), Pozzolana (P) i Feldspar, koji su primenjeni za obradu morske vode. Rezultati istraživanja ukazuju da se procenat adsorpcije smanjuje sa povećanjem početne koncentracije, dok se aktuelna količina adsorbovanih jona po jedinici mase adsorbenta povećava sa povećanjem koncentracije jona metala. Vrednosti  $\Delta G$  su negativne u granicama od 21 do 26 kJ/mol, dok su vrednosti  $\Delta H$  i  $\Delta S$  pozitivne u opsegu 0,1 do 25 kJ/mol. Vrednosti  $\Delta H$ ,  $\Delta S$  i  $\Delta G$  ukazuju na favorizovanu fizičku adsorpciju i pokazuju da LDH/T-P-F kompoziti imaju značajan potencijal kao adsorbenti za uklanjanje jona iz morske vode.*

*Ključne reči: predretman; morska voda; keramiči filteri; Tripoli; Pozzolana; Feldspar.*