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STUDY OF THE ADSORPTION EFFICACY OF Cr (III) ON A METAL OXIDE-BASED MATERIAL DERIVED FROM THE QUARTZ SAND ENRICHMENT PROCESS.

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Abstract

In the present study, a metal oxide based material, derived from the enrichment process of quartz coastal sand was used as adsorbent for the removal of chromium (III). Following additional modification of the adsorbent, the effect of operational parameters including pH, contact time and Cr (III) concentration were studied according to one-factor-at-a-time procedure. Obtained results revealed that selected material exhibited higher adsorption efficacy in alkaline solution (pH = 6-9). The maximum removal efficacy (>93%) was achieved after 180 minutes of contact time, adsorbent dosage 5 g/L and initial chromium concentration 20 mg/L. The adsorption isotherms were better described by the Freundlich equation (R^2 = 0.934). Adsorption of trivalent chromium ions onto selected material followed the pseudo second order model (R^2 = 0.996). Hence, the residual materials derived from the enrichment processes of quartz sand can be used as alternative adsorbent for the removal of trivalent chromium ions from aqueous solutions.

Key words: metal oxide, chromium (III), adsorption efficacy, adsorption isotherms, batch experiments

1. Introduction

The use of solid adsorbents as important tools for the removal of heavy metals from polluted water and soil sites has gain increasing attention in the recent years (Fabbricino et al., 2013). The persistence of these contaminants in the environment requests for affordable materials, among which natural ones are of great interest (Allen et al., 1989; Nikagolla et al., 2013; Elabbas et al., 2016; Griffin et al., 1977; Gupta et al., 2001; Malamis et al., 2013). With the rapid development of metal processing industries, heavy metals are directly or indirectly discharged into the environment increasingly, especially in countries under development (Mohan et al., 2006; Shehu et al., 2011).

Toxic metals are not biodegradable and very persistent and hence their concentrations need to be reduced to acceptable levels prior to their discharge in water or soil (Susaj et al., 2017; Shehu et al., 2011). Chromium toxicity is greatly dependent by a variety of chromium compounds, its oxidation state and its solubility in water (Bademo et al., 2016; Fiol et al., 1977). In the environment chromium mostly occurs as a trivalent ion, which is known for its essential properties while hexavalent chromium, despite its higher liability and availability in the environment, is considered highly toxic and exhibits mutagenic and carcinogenic activity (Kara et al., 2012; Mandal et al., 2015; Bueno et al., 2008). In certain conditions, in the presence of oxidizing agents, trivalent chromium can easily be oxidized to hexavalent chromium (Kara et al., 2006).

The use of metals oxide based natural materials can be an efficient and cost-effective method of chromium removal from contaminated water and soils (Reddy et al., 2013; Mandal et al., 2015). Similar studies conducted for this purpose have shown promising adsorption capacities for chromium removal efficacy (Gupta et al. 2001; Bademo et al., 2016; Reddy et al., 2013).

Albania is rich in mineral resources, among which Bulqiza ultrabasic massif is the biggest chrome-potential massif, ranked fourth in the world for chrome reserves (Susaj et al., 2017). More than 136 entities develop chromium exploitation mining activity in the district of Bulqiza city, which has been accompanied by significant adverse impacts on the quality indicators of soil and water in the surrounding area due to excavation of chrome ore inside the galleries, as well as the rinsing of mineral stocks and sterile wastes loaded with Cr dust at the storage facilities (Susaj et al., 2017). Since now days, studies have been focused mainly in identifying the state of contamination with chromium in the areas of concern while only few studies imply efforts on the use of solid adsorbents for remediation processes (Susaj et al., 2017).

The aim of this work was to study the effect of a metal oxide based material, derived from the enrichment process of quartz coastal sand was used as adsorbent for the removal of chromium (III) ions from solution.

2 Materials and Methods

2.1 Treatment of adsorbent material

The natural metal oxide based mineral was collected in the former "Coastal Sand Enrichment Factory" in the area of Shijak Road, Durrës. A representative quantity of the material (about 2 kg) was collected in the field from different piles disposed in the area. The representative sample was further processed in the laboratory by finely grinding in agate mortar, until the ore was finely grounded and physically resembled in a powdered material. Than the material was passed through sieves with different fractions and the 0.063 mm fraction was used in study.

Sieved material was activated with sulfuric acid, H_2SO_4 10%. The treatment was performed in plastic tubes, where a certain amount of the material was left in contact with 10% sulfuric acid for about 4 hours. Than the material was rinsed several times by decantation with deionized water until the pH = 5.5 and dried at 105 ± 5^oC.

3 Batch equilibrium studies

3.1 Effect of pH

To study the effect of pH on the process of Cr(III) ions adsorption, a series of standard solutions was prepared and treated with selected material at different pHs, respectively: 3-3.5; 5.5-6 and 9. The pH of the solutions was adjusted by using either a buffer solution or 0.1M NaOH solution.

For this purpose, about 0.05 g of metal oxide material was mixed with 10 ml of Cr(III) standard solution for 24 hours, centrifuged for the best possible separation of solid particles and transferred to clean containers. Determination of the residual Cr(III) concentration in solutions was performed by using the flame atomic absorption spectroscopy technique, SAAF. All solutions were acidified with nitric acid, HNO_3 prior to the determination of chromium concentration.

3.2 Effect of contact time and adsorption kinetics of Cr(III)

The study of the adsorption kinetics was performed by treating the adsorbent with standard solutions of Cr(III) of same concentration (5ppm), at pH 8-9. For this purpose, 9 solutions were prepared by adding 0.05 g of metal oxide material in 10 ml of standard solution. Solutions were placed in rotating shaker for different time intervals. After removing from the shaker, solutions were left to stand for a few minutes to decant and then were centrifuged. Solutions were acidified with nitric acid, HNO_3 prior to the determination of Cr concentration.

The pseudo first-order adsorption kinetics model is given by the equation (Ho et al., 1999; Mustafa et al., 2010):

$$\log (qt - qe) = \log(qe) - k_1 \cdot t / 2.303$$

where "q_t" and "q_e" represent the amount of adsorbed chromium expressed in ($mg.g^{-1}$) respectively at time "t" and in equilibrium and k_1 represents the first order reaction rate. The straight line of log (qt-qe) versus t has an intercept a = log (qe) and the slope b = k1 /2.303.

The kinetic model of the second order reaction is given by the equation

$$t/qt = 1/k_2 q_e^2 + (1/qe) \cdot t$$

Initial rate of the reaction is given by the formula:

$$h = k_2 \cdot q_e^2$$

where, k_2 is the rate constant of the equation and "qt" quantity adsorbed in time "t".

3.3 Adsorption isotherms of Cr(III)

For this purpose, 0.05 g of the material was treated with standard solutions with different concentrations of Cr(III), ranging from 4 - 200 mg/l at pH 8-9. The treated samples were placed in the rotary shaker for 12 hours and then left for several minutes to rest and decant. After decantation, they were centrifuged and transferred to clean containers where the solutions were diluted so that their concentration fall within the linear working area, and then 0.05 ml of nitric acid was added. The concentration of Cr remained in each solution was calculated by the calibration curve method, using the SAAF technique. From the obtained results, the amount of chromium adsorbed per unit weight, “qe” and the equilibrium concentration of chromium present in the solution, “Ce” were calculated.

3.4 Langmuir isotherm

The Langmuir isotherm is used in cases when a monomolecular layer adsorption is suggested. The theory is based on the assumption that there are a finite number of binding sites that are homogeneously distributed over the adsorbent surface, and once the adsorbate occupies a site, no further adsorption can take place at that site (Ezzati, 2020; Irdemez, 2021). Adsorption capacity of Cr^{3+} in the natural material was studied by the Langmuir equation, as below:

$$\frac{\mathrm{Ce}}{\mathrm{qe}} = \frac{\mathrm{Ce}}{\mathrm{qm}} + \frac{1}{\mathrm{KLqm}}$$

where K_L and q_m are the Langmuir adsorption constant (L/mg) and the maximum adsorption capacity (mg/g) respectively. K_L represents the affinity between the adsorbate and the adsorbent. The main parameters of the Langmuir isotherm can be used to predict the affinity between the adsorbate and the adsorbent through the separation factor RL which is calculated by the formula:

$R_L = (1/1 + K_L \cdot C_{0\ \mathrm{max}})$

The value of the R_L factor provides important information about the nature of the adsorption process. The R_L value must be between 0 and 1 for a favored adsorption. If RL> 1, adsorption is not favorable and when RL = 1 then adsorption is linear. When RL = 0 adsorption is irreversible.

3.5 Freundlich Isotherm.

Freundlich isotherm is applied when it is assumed that the adsorption process occurs on heterogeneous surfaces (Ezzati R, 2020). Freundlih's linearized equation is given by the equation:

$\log q_e = \log K_F + \frac{1}{n} \log C_e$

where
q_e –the adsorbed quantity of Cr(III) in adsorbent (mg/g)
C_e – concentration of Cr(III) remained in solution (mg/L)
K_F – Freundlich constant or the adsorption capacity constant (L/mg)
n – a quotient which represents the intensity of the adsorption process.

4. Results and Discussions

4.1 Effect of pH and contact time

In the Figure 1 the obtained results regarding the optimal pH and contact time for maximum removal efficacy of Cr(III) from solution are presented.

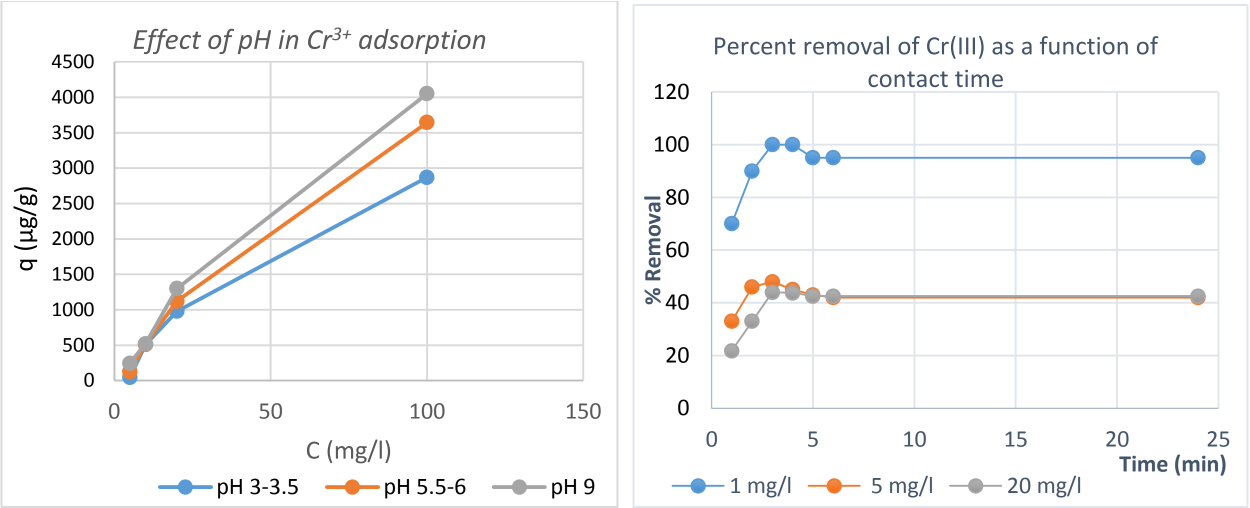

Figure 1. Adsorption efficacy of Cr(III) at different pH and contact time.

Discussion: The amount of adsorbed Cr(III) (in µg/g adsorbent) increases with increasing the pH in solution. The influence of pH was most noticeable when the concentration of Cr(III) ions in solution is low (respectively, 5 ppm) compared to more concentrated solutions. Thus, the amount of Cr(III) adsorbed increases by about 3 times from pH 3 to pH 6 and about 6 times from pH 3 to 9, for the 5 ppm solution.

When the concentration of Cr(III) in solution is low, the adsorption efficiency increases because of the higher number of free active centers located on the surface of the metal oxide material. The greater adsorption efficacy in alkaline solution can be explained by the fact that the OH^- groups predominate on the surface of the metal oxide material. So the surface of the material is negatively charged and this causes electrostatic attraction to occur between the surface of the metal oxide and the Cr(III) ions. These conclusions are consistent with previous studies showing that cations in solid materials consisting mainly of metal oxides are better adsorbed in alkaline solution while anions are better adsorbed in acidic solution, assuming an electrostatic attraction between active centers and ions in solution (Allen et al., 1989; Plazinski 2009; Wiśniewska et al., 2013).

Discussion: There is a rapid increase in the amount of adsorption of Cr(III) ions in the solid material in the first 30 to 60 minutes, an increase which remains constant for up to 180 minutes treatment. The rapid adsorption of Cr(III) in the first 30 min occurs due to the presence of free centers located on the surface of the material. Maximum adsorption capacity is reached in 1-3 hours and is approximately 0.45 mg/g. Then, since the free active centers are occupied by Cr(III) ions, a state of equilibrium is reached between the amount of Cr adsorbed and that remaining in the solution, so the adsorptive saturation of the material surface occurs over time. This means that the optimal treatment time of the material should extend to the area where the equilibrium state is reached between the amount of adsorbed analyte and its amount remaining in the solution, so the solutions are recommended to be treated with the metal oxide material for more than 4 hours.

4.2 Adsorption kinetics

Results obtained with regard to the kinetics of Cr (III) adsorption are presented in table below and are illustrated graphically in Figures 2 and 3.

Table 1. Study of the adsorption kinetics of Cr (III)

Time t (h)	0.5	1	2	3	4	5	6	24	24
Adsorbed quantity qt (mg/g)	0.09	0.43	0.47	0.46	0.35	0.33	0.32	0.3	0.31
t/qt	5.56	2.33	4.26	6.52	11.43	15.15	18.75	80.00	77.42
qe-qt	0.38	0.04	0.00	0.01	0.12	0.14	0.15	0.17	0.16
log(qe-qt)	-0.42	-1.40		-2.00	-0.92	-0.85	-0.82	-0.77	-0.80

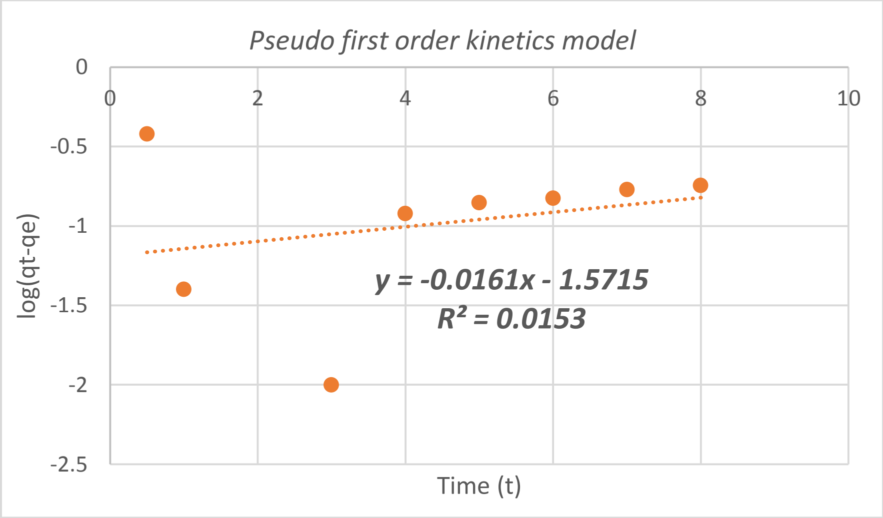

Figure 2. *Pseudo First order kinetics model*

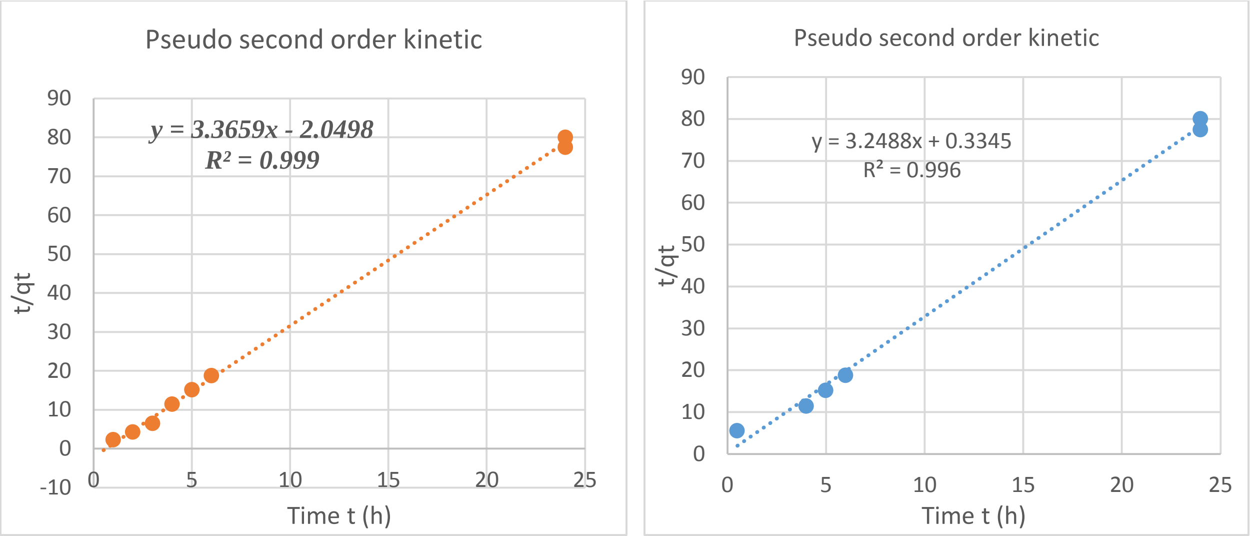

Figure 3. *Pseudo second order kinetics model*

Discussion: From the obtained results it is concluded that the value of the intercept of the equation which represents the term $1 / k_2 \cdot qe^2$ resulted to be a negative value. The reason may be the rapid increase in the amount of Cr(III) adsorbed in the first hours and then the decrease until equilibrium was reached. For this purpose, the graph was re plotted using only the values of the measurements in equilibrium.

Table 2. Calculations of the adsorption kinetics

Pseudo first order kinetics			**Pseudo second order kinetics**			
R^2	k_1 (min^{-1}) $b \cdot 2.303$	Calculated Equilibrium concentration , 10^a	R^2	k_1 (g/mg·min) $1/a \cdot qe^2$	Calculated Equilibrium concentration, qe=1/b	$h=k_2 \cdot qe^2$ (g/mg·min)
0.0153	0.037	0.027 mg/g	0.996	9.7	0.31 mg/g	0.93

Discussion: Through the obtained results regarding the adsorption kinetics it was concluded that the second order pseudo reaction model responds better to our results as in this case the value of the linearity coefficient has been quite high, $R^2 = 0.996$. The reaction rate resulted 9.7 g mg^{-1} min^{-1} and the initial rate of adsorption process was h = 0.93 g/mg.min. The equilibrium concentration calculated through the second order kinetic model resulted in 0.31 mg/g.

With the results obtained in the Table 3, the graph of the isotherm of adsorption of Cr(III) ions in the natural material was plotted as a dependence of the amount of Cr(III) ions adsorbed per unit mass of solid material (mg/g) versus the equilibrium concentration of Cr(III) ions, (Figure 4).

Table 3. Results of the Cr(III) adsorption.

C_0 (mg/L)	C_e (mg/L)	q_e (mg/g)	qe (%)	c_e/q_e	Log c_e	Log q_e

0.5	0.0	0.10	100.00	0	-	-
1.0	0.00	0.20	98.00	0	-	-0.69
2.0	0.14	0.23	93.00	2.64	-0.85	-0.64
4.0	2.57	0.29	35.75	8.99	0.41	-0.54
8.0	4.83	0.63	39.63	7.62	0.68	-0.20
10.0	7.00	0.60	30.00	11.67	0.85	-0.22
20.0	11.19	1.76	44.05	6.35	1.05	0.25
50.0	41.49	1.70	17.02	24.39	1.62	0.23
100.0	82.69	3.46	17.31	23.88	1.92	0.54
150.00	123.58	5.28	17.61	23.39	2.09	0.72
200.00	162.99	7.40	18.51	22.02	2.21	0.87

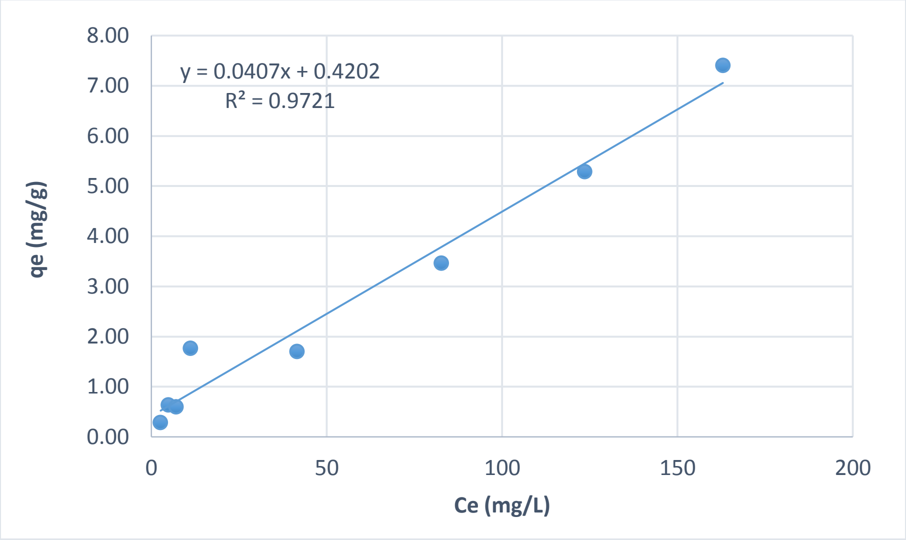

Figure 4. Graph of the dependence of the adsorbed amount of Cr(III) *ions per unit mass of solid material versus the equilibrium concentration of* Cr(III) *ions.*

Discussion: Obtained results show that the amount of Cr(III) ions adsorbed per unit mass of solid material, expressed in mg/g, increases with the increase concentration of Cr(III) in solution. The amount of metal oxide used, approximately 0.05 mg was able to adsorb all the amount of chromium contained in the initial solution, for chromium concentrations ranging from 0.5 - 2.0 mg/L where the amount of chromium removed from the solution varied from 93 - 100%. As the chromium concentration increases, the percentage of chromium removed decreased and varied from approximately 20% to 44% of the initial concentration. It can also be concluded that the highest adsorption efficiency was achieved for chromium concentration of 20 ppm or for the chromium concentration/mass of material ratio is about 400.

The maximum amount of chromium adsorbed on the metal oxide material reached 7400 μg/g or 7.4 mg/g. The amount of adsorbed Cr^{3+} increased with increasing concentration and up to the initial concentration of chromium 200 mg/L we can say that the state of absorption saturation is not reached as the coefficient of linearity of the adsorption curve is quite high, $R^2 = 0.9721$.

4.3 Langmuir isotherm

Langmuir isotherm was plotted according to the equations given in 3.4. Results are presented in the graph of Figure 5.

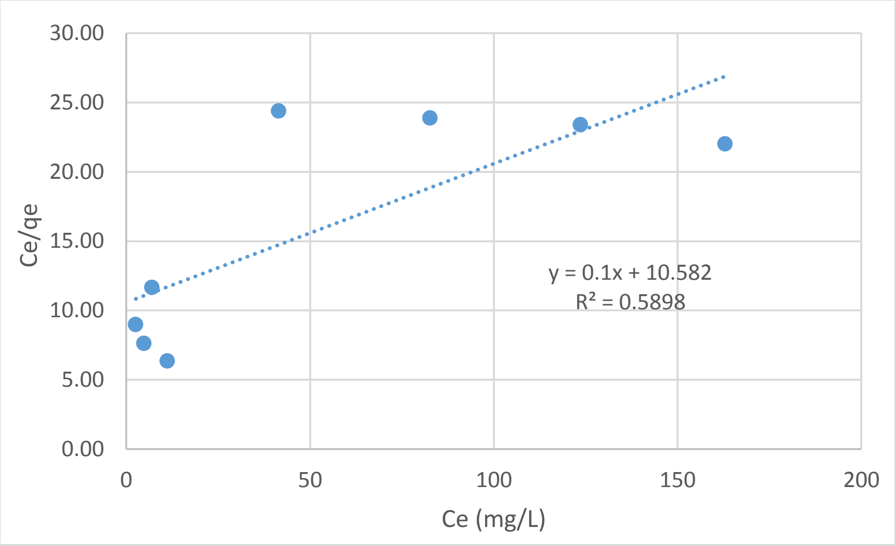

Figure 5. Linearized model of Langmuir adsorption isotherm of Cr(III).

From the equation we can calculate the value of K_L and q_m :

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

$b = 1/q_m \rightarrow q_m = 1/b$
$q_m = 1/b = 1/0.1 = 10$ (mg/g)
$a = 1/q_m \cdot K_L \rightarrow K_L = 1/q_m \cdot a$
$K_L = 1/\ 10 \cdot 10.582 = 0.0095$ (L/mg)

Separation factor R_L can be calculated using the formula:

$R_L = (1/1 + K_L \cdot C_{0\ max})$

where : Co_{max} is the maximum initial concentration of Cr(III) ions in solution:

$R_L = (1/1 + 0.0095 \cdot 200) = 0.34$

$(0 < R_L < 1)$

Discussion: The value of the correlation coefficient has resulted $R^2 = 0.5898$. This low value of the correlation coefficient indicates that the adsorption of Cr(III) ions in the metal oxide material cannot be explained by the Langmuir's theory. By calculating parameters such as the maximum adsorption efficiency or Langmuir constant it resulted that the maximum adsorption capacity of chromium in solid material, qm resulted 10 mg/g, a value approximately equal to the value 7.4 obtained from the adsorption curve.

Langmuir constant, K_L which characterizes the affinity of the adsorbent to the adsorbate has resulted 0.0095 L / mg and the factor $R_L = 0.34$ which indicates that this adsorbent has a medium affinity to the adsorbate, ie trivalent chromium.

4.4 Freundlich Isotherm.

The graph below shows the linearized model of Friendlich isotherm.

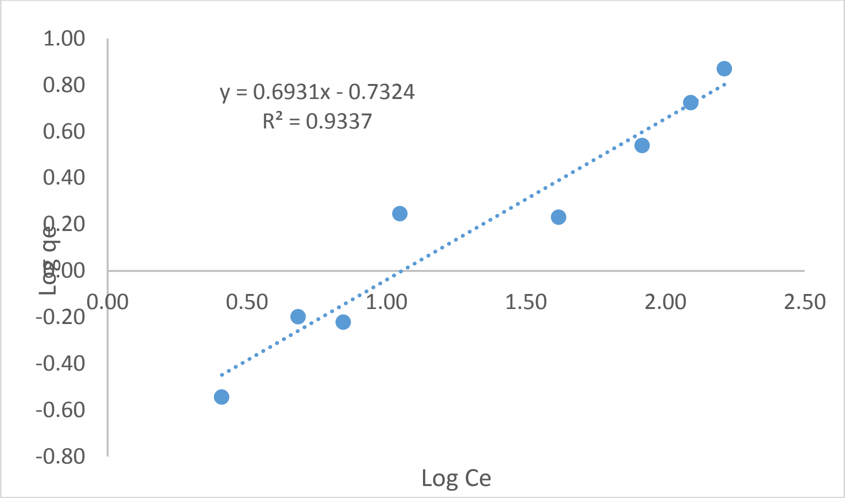

Figure 6. Linear graph of Freundlih adsorption isotherm for Cr (III) ions.

Discussion: Obtained results from Frenudlih's linearized isotherm regarding the adsorption of Cr(III) ions in solid material we reach to the following conclusions:
The value of the correlation coefficient $R^2 = 0.9337$. As we see the value of the correlation coefficient in the case of the Freundlich adsorption isotherm is greater than that calculated in the Langmuir isotherm. This shows that the adsorption of Cr(III) ions in the metal oxide material conforms to Freundlih's theory. So the adsorption of Cr^{3+} ions in the solid material is not associated with the formation of a monomolecular layer on the surface of the particles of the material, but by the creation of heterogeneous layers. The formation of heterogeneous layers on the adsorbent surface is a characteristic of physical adsorption. During physical adsorption the interaction of adsorbent and adsorbate is realized by means of vandervalsian forces. These adsorbent forces ensure the attraction of atoms (molecules). From the Freundlich linearized equation we calculate the value of KF and n .

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

$$a = \log K_F \rightarrow KF = \text{antilog } a$$

$$K_F = \text{antilog } (-0.7324) = 0.19 \text{ (mg/g)}$$

$$1/n = b \rightarrow n = 1/b$$

$$n = 1/0.6931 = 1.4$$

Values of the Langmuir and Freundlich constants for the adsorption of Cr(III) ions in the solid material material are presented below.

Type of Isotherm	**Langmuir**				**Freundlich**		
Metal ion	q_m (mg/L)	K_L (L/mg)	R_L	R^2	K_F (mg/g)	n	R^2
Cr^{3+}	10	0.0095	0.34	0.5898	0.19	1.4	0.9337

Discussion. Through the results obtained regarding the character of the adsorption process of Cr(III) ions in the metal oxide material we can say that the experimental values obtained fit better with the Freundlich isotherm model of adsorption. This is because the correlation coefficient was high, $R^2 = 0.9337$ compared to the Langmuir model of the adsorption isotherm where $R^2 = 0.5898$. This means that the process of adsorption of Cr(III) ions in the solid material is not homogeneous and Cr is not adsorbed only in a monomolecular layer.

Conclusions

Natural metal – oxide material, derived from the enrichment of the quartz coastal sand process removes Cr(III) ions from solution by the main mechanism, adsorption. Optimal adsorption conditions were determined in batch experiments, using the one-factor-at-a-time procedure. Experimental results were evaluated with Langmuir and Freundlich isotherms. The adsorption process for Cr(III) follow the Freundlich isotherm and gives high correlation coefficient $R^{2.}$ Calculations performed based on the Langmuir isotherm showed that the maximum adsorption efficiency of Cr^{3+} in the natural metal-oxide material has resulted 10 mg/g or 10000 μg/g. Pseudo second order reaction kinetics has provided a realistic description for removal of Cr(III) from solution with high correlation coefficient R^2 of (0.999). However, further studies concerning different interferences that influence maximum adsorption capacity of Cr(III) ions in selected material should be carried aiming to improve the adsorption process.

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