Experimental and theoretical investigations for the removal of chromium (III) from aqueous solutions using sugarcane bagasse

K . Al-Mokhalelati[*] **Dr. I.M. Al-Bakri**[*]
Dr. N.H. AlShibeh AlWattar[*]

Abstract

The isotherms behavior via Langmuir, Freundlich and Temkin isometric models are investigated. Langmuir shows within the studied concentrations of chromium(III) that the adsorption has no any effect, Freundlich shows that the adsorption process occurs on heterogeneous surfaces has an exponential distribution of the active sites and their energies indicating the heterogeneity of the relative energy distribution within the adsorption sites. Temkin isometric model, where the interaction between the adsorbent material and the active sites of the adsorbent has emphasized the nature of the adsorption between the chromium (III)and the sugarcane bagasse through b = -ΔH and determined the type of chemical adsorption as Temkin's calculated results using solver. ANOVA matched the experimental results. Two-Factor affecting the results of industrial water treating the containing the ion (Cr^{3+}) with a variation in the efficacy of the treatment when the concentration of the chromium ion changed (from 600 to 3000 ppm) or the material used in the changed treatment of (SB-N or SB-KOH) and KOH-SB outperformed N-SB at all

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[*] Department of Chemistry, Faculty of Science, University of Damascus, Damascus, Syria.

applied conditions. The internal diffusion equation shows that the adsorption of chromium (III) on the SB-KOH surface is governed by two phases of the outer mass transfer (boundary layer diffusion) and (the internal diffusion phase) within the pores of the absorbent. The theoretical study showed that the mechanism of chromium (III) binding with alginate Cr^{3+}-alginate bond cannot be electrostatically linked, because of the bond length in the formed complex which is smaller than the sum of the two diameters Cr^{3+} and O^{2-}. This explains the isotherm results of Freundlich and Langmuir due to the increase of the maximum adsorption capacity q_m and the proportion of chromium(III) retention time at high concentrations forming a strong bond allowing to retain chromium(III) in sugarcane bagasse and thus form complexes between chromium(III) and alginate (COO^-, O^{2-}).

Keywords: Sugarcane bagasse, Adsorption, Chromium (III), Alginate DFT / B3LYP method.

دراسات نظرية وعملية لإزالة الكروم الثلاثي من محاليل مائية باستعمال مخلفات عصر قصب السكر

كمال فريد المخللاتي[*] **د. إيمان مصطفى البكري**[***]

د. نسرين حسن الشبه الوتار[***]

الملخص

تم التحقيق في سلوك متساوي درجة الحرارة عبر نماذج Langmuir وFreundlich وTemkin. وضح Langmuir ضمن التراكيز المدروسة من الكروم (III) أن الامتزاز ليس له أي تأثير، وضح Freundlich أن عملية الامتزاز تحدث على الأسطح غير المتجانسة ولها توزيع أسي للمواقع النشطة وطاقاتها تشير إلى عدم تجانس توزيع الطاقة النسبي داخل مواقع الامتزاز، في حين أكد نموذج Temkin التفاعل بين المادة الممتزة والمواقع النشطة للمادة الممتزة على طبيعة الامتزاز بين الكروم (III) ومخلفات قصب السكر من خلال $b = -\Delta H$ وكان طبيعة الامتزاز كيميائي حسب Temkin. وبين وجود تطابق بين الدراسة الإحصائية ANOVA والنتائج التجريبية. عاملان يؤثران على نتائج

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[*] طالب ماجستير، قسم الكيمياء، كلية العلوم ، جامعة دمشق.

[**] أستاذ مساعد، قسم الكيمياء، كلية العلوم ، جامعة دمشق.

[***] مدرس، قسم الكيمياء، كلية العلوم ، جامعة دمشق.

معالجة المياه الصناعية المحتوية على الأيون (Cr^{3+}) مع اختلاف في فعالية المعالجة عندما يتغير تركيز أيون الكروم (من 600 إلى 3000 جزء في المليون) أو المادة المستعملة في المعالجة. تفوقت (SB-N أو SB-KOH) و KOH-SB على أداء SB-N في جميع الظروف المطبقة. توضح معادلة الانتشار الداخلي أن امتزاز الكروم (III) على سطح SB-KOH يخضع لمرحلتين من نقل الكتلة الخارجية (انتشار الطبقة الحدودية) و (مرحلة الانتشار الداخلي) داخل مسام المادة المازة. أظهرت الدراسة النظرية أن آلية ارتباط الكروم (III) مع الرابطة الجينية Cr3 + alginate- لا يمكن ربطها إلكتروستاتيكيا ، نظرا لطول الرابطة في المركب المتشكل وهو أصغر من مجموع القطرين Cr^{3+} و O^{-2}. وهذا ما يفسر نتائج متساوي درجة الحرارة لـ Freundlich و Langmuir بسبب زيادة قدرةالامتزاز الأعظمية q_m ونسبة زمن الاحتفاظ بالكروم (III) بتراكيز عالية مكونة رابطة قوية تسمح بالاحتفاظ بالكروم (III) في مخلفات عصر قصب السكر وبالتالي تكوين معقدات بين الكروم (III) والجينات (COO^-، O^{-2}).

INTRODUCTION:

As a result of growing industrial activity, many chemicals such as heavy metals, organic compounds and synthetic materials pose serious contamination and deterioration damage problems to the environment[1,2]. Chromium is a heavy metal causing many problems during wastewater treatment. Chromium (III) is found naturally in small quantities in the body, and performs important functions, particularly concerning glucose metabolism[3,4]. Nevertheless, prolonged exposure to trivalent species may also cause skin allergies and cancer in human beings[5,6].Studies on the development of effluent treatments containing heavy metals have indicated that adsorption is a highly effective and inexpensive alternative process among the various available treatments for removing heavy metal ions[7]. In recent years, many studies have been carried out to evaluate the effectiveness of various methods for removing of large amounts of chromium from industrial effluents using economically viable adsorbents based on agro-industrial residues, such as carrot residues, raw rice bran, vineyard pruning waste, bacteria from tannery effluent contaminated soil and castor seed hull[8,9]. Adsorption of heavy metals by agro-industrial residues is commonly called biosorption; it describes a property of the non-living biomass to retain metal ions as a result of electrostatic interactions and complex formations between these ions and functional groups present in the biomass[10]. The mechanisms responsible for the interaction of metal ions with the structure of these materials are determined by the identification of functional groups, such as carboxylate, phosphate and amino groups, which are typically important for the biosorption process[11,12]. For instance, chemically modified sugarcane bagasse, which is an agro-industrial residue are widely available and has been recently employed for the adsorption of copper, cadmium, lead, nickel, zinc, magnesium and calcium from aqueous solutions[13].

The aim of the present work is to explore the ability of using sugarcane bagasse based on adsorbent natural material for removing chromium (III) from aqueous solution including a theoretical study on the mechanism of the triple chromium (III) with the cellulosic structure interference of sugarcane bagasse material.

EXPERIMENTAL

Reagents

Analytical grade chemical reagents were used in this study. A 3000 mg L^{-1} chromium stock solution was prepared from Chromium Chloride $CrCL_3$ from Vetec, with 98% concentration, and required dilutions were carried out using deionized water. Also, a 0.3 N KOH solution was used.

Metal adsorption experiment

Adsorption as a function of time

The adsorption of chromium (III) ions, on the modified bagasse on both SB-N and SB-KOH with were carried out. A stock solution of chromium (III) at the concentration of 3000 mg L^{-1} was prepared using analytical grade material of Chromium Chloride ($CrCl_3$) taking 15.372 g and dissolved in 1000 mL of distilled water

Spectrophotometric measurements of chromium (III) concentration were recorded on optizen 322OUV at the maximum wavelength absorption at 420 nm. The calibration standards of chromium (III) in the linear dynamic range of (600-800-1000-1500-2000-2500- to 3000) mg L^{-1} were used to calibrate the UV-Visible spectrophotometer. The lower limit of correlation of determination (R^2) of 0.99 was used to ensure linearity. The initial and equilibrium concentrations in solution were measured and the amount of chromium (III) adsorbed on the SB-N,SB-KOH was also calculated from the mass balance equation 1 given below:

$$Q_e = \frac{V\,(C_i - C_e)}{m} \qquad (1)$$

The percentage removal was calculated using equation 2.

$$\%\mathbf{Removal} = \frac{C_i - C_e}{C_i} \qquad (\ 2\ )$$

Where C_i and C_e are the initial and equilibrium concentrations of chromium (III) in mg L^{-1} respectively, Q_e is the amount of chromium(III) adsorbed at equilibrium in (mg/g,) V is the volume of the chromium solution (L) and m is the mass of the SB-N,SB-KOH in (grams).

The internal diffusion equation

The diffusion mechanism can be explained using the internal diffusion model, where the internal diffusion depends on several factors such as physical properties of the adsorbent, the initial concentration of the adsorbent, the temperature and the mixing speed in the static method [14]. Weber and Morris proposed the equation for endogenous diffusion represented by the relationship whereas, Ki represents the internal diffusion velocity (mg /g $\min^{1/2}$) and C diffusion layer thickness:[14,15]

$$q_t = K_i t^{1/2} + C \qquad (3)$$

By drawing the graph that represents the relationship between q_t , $t^{1/2}$, a straight line passing through the principle is obtained, this indicates the internal diffusion phase within the pores of the adsorbent, which is the specific step of the adsorption rate [15].Theoretically, the graph line should show at least four linear regions representing the boundary propagation stage, followed by internal propagation within pores of the macro, meso, or micro order, and these four regions are followed by a horizontal line representing the arrival to the equilibrium state [16].

Theoretical study

A theoretical study was carried out using the DFT / B3LYP method in the NWCHEM[17] program in order to find out the method of correlation between chromium(III) and functional groups (COO^-, OH) in alginates.

RESULTS AND DISCUSSION

Five models were used isotherm parameters which were obtained using the Langmuir method for chromium (III) adsorption on (SB –N, SB-KOH).

$$\frac{1}{C_e} = -K_L + K_L q_m \frac{1}{q_e} \qquad (4)$$

$$\frac{q_e}{C_e} = K_L q_m - K_L q_e \qquad (5)$$

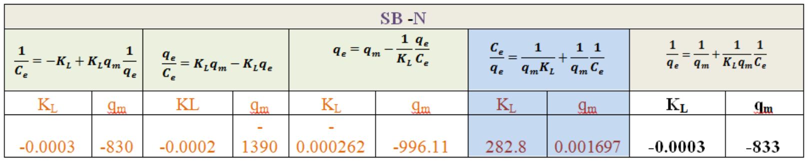
$$q_e = q_m - \frac{1}{K_L}\frac{q_e}{C_e} \qquad (6)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m}\frac{1}{C_e} \qquad (7)$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m}\frac{1}{C_e} \qquad (8)$$

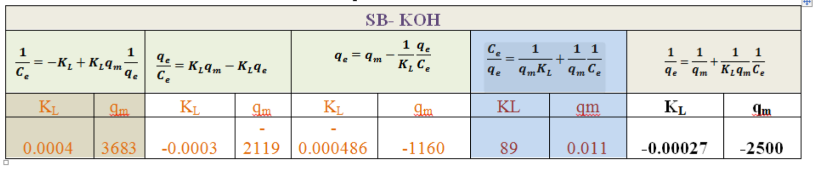
Table 1.2 shows the Langmuir results within the studied concentrations of chromium (III) adsorption. It does not apply to chromium adsorption on sugarcane bagasse (SB –N, SB- KOH) as expected, the Langmuir model assumes that adsorption forces are similar to chemical reactions, and there is no interaction between adsorbed species but only between these species and the adsorbent. Furthermore, adsorption on the adsorbent surface occurs up to the formation of a single, uniform layer (monolayer) [18].

Table. 1 Isotherm parameters obtained using the Langmuir method for chromium (III) adsorption on SB -N



SB -N									
$\frac{1}{C_e}=-K_L+K_Lq_m\frac{1}{q_e}$		$\frac{q_e}{C_e}=K_Lq_m-K_Lq_e$		$q_e=q_m-\frac{1}{K_L}\frac{q_e}{C_e}$		$\frac{C_e}{q_e}=\frac{1}{q_mK_L}+\frac{1}{q_m}\frac{1}{C_e}$		$\frac{1}{q_e}=\frac{1}{q_m}+\frac{1}{K_Lq_m}\frac{1}{C_e}$	
K_L	q_m	KL	q_m	K_L	q_m	K_L	q_m	K_L	q_m
-0.0003	-830	-0.0002	-1390	-0.000262	-996.11	282.8	0.001697	**-0.0003**	**-833**

Table. 2 Isotherm parameters obtained using the Langmuir method for chromium (III) adsorption on SB- KOH



SB- KOH									
$\frac{1}{C_e}=-K_L+K_Lq_m\frac{1}{q_e}$		$\frac{q_e}{C_e}=K_Lq_m-K_Lq_e$		$q_e=q_m-\frac{1}{K_L}\frac{q_e}{C_e}$		$\frac{C_e}{q_e}=\frac{1}{q_mK_L}+\frac{1}{q_m}\frac{1}{C_e}$		$\frac{1}{q_e}=\frac{1}{q_m}+\frac{1}{K_Lq_m}\frac{1}{C_e}$	
K_L	q_m	K_L	q_m	K_L	q_m	KL	qm	K_L	q_m
0.0004	3683	-0.0003	-2119	-0.000486	-1160	89	0.011	**-0.00027**	**-2500**

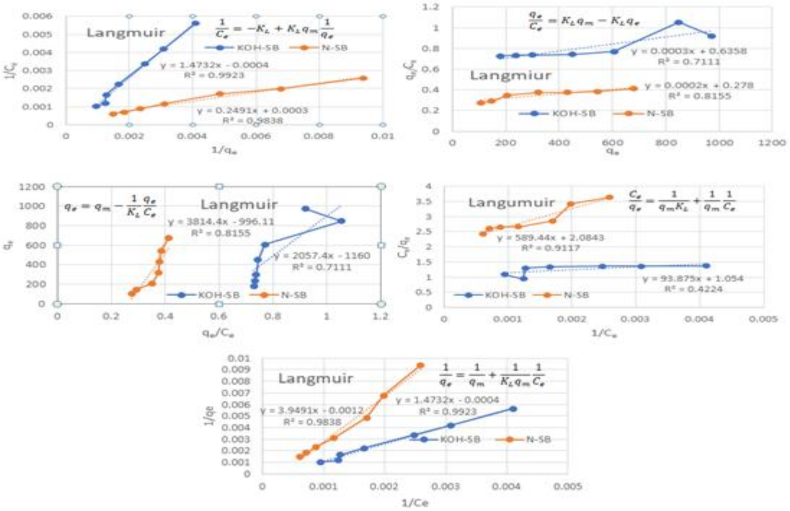


Figure 1. : Isotherm parameters using the Langmuir method for chromium (III) adsorption on

SB –N, SB- KOH.

Table. 3 show the Langmuir constants were determined using the Excel program the solver property, as the results confirming all the results (by applying the linear relationships of the Langmuir and the solver application) that the studied adsorption does not apply to the Langmuir equation. However, the striking thing is that the maximum adsorption capacity q_m was significantly increased after treating sugarcane bagasse with KOH.

Table. 3 The Langmuir constants were determined using the Excel program the solver property.

Equal to Langmuir solver	**R_L**	**K_L**	**q_m**
SB- KOH	**Adsorption is not preferred**	3.36691E-05	26760.36095
SB –N	favorite	0.023198	11.99979

Table. 4 show the isometric of Freundlich using adsorption process occurring on heterogeneous surfaces and with an exponential distribution of the active sites and their energies, and indicate the heterogeneity of the relative energy distribution within the adsorption sites. Kf represents the adsorption capacity (L/mg) and (1/n) the adsorption density (usually values of 1/n range between 0 and 1), which is a term indicating the strength of adsorption and n depends on the nature of the adsorption and on the temperature, as the equilibrium of Freundlich fails at high pressures.

Table. 4 Isotherm parameters obtained using the Freundlich method for chromium (III) adsorption on SB –N, SB- KOH

Freundlish equal	R^2	n	1/n	K_f
SB- KOH	0.9739	0.843384	1.1857	0.041362
SB –N	0.9935	0.797	1.2553	0.0628

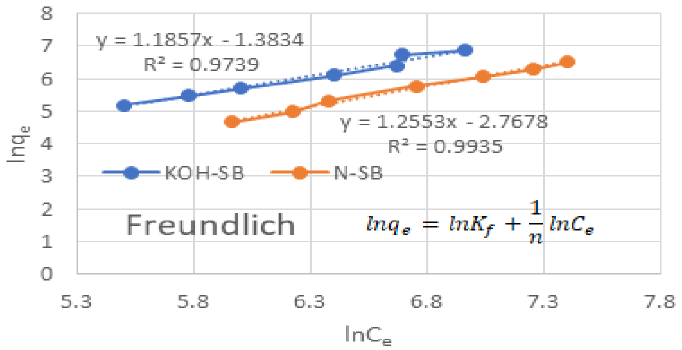


Figure 2.: Isotherm parameters the Freundlich method for chromium (III) adsorption on SB –N, SB- KOH.

Table. 5 shows the Freundlich determined constants using the Excel program and the solver property, as the results confirming all the results (by applying the linear relationships of the Langmuir and the solver application) the results were that, although the Freundlich curve gives good linearity, this is not sufficient because the values of n <1 and that due to the high concentration of the adsorbed pigment on the adsorbent, the Freundlich model fails at high concentrations.

Table. 5 The Freundlich constants were determined using the Excel program the solver property

Equal to Freundlich solver	N	1/n	K_f
KOH-SB	0.811148	1.233	0.185694
N-SB	0.831408	1.203	0.090518

The internal diffusion equation relationship (3) was applied to the results of the chromium (III) ion adsorption at different times and concentrations of SB-KOH recorded in Table 6. Figure 3 shows the graphical curve representing the application of this equation. It was noted that all the graphs do not pass from the principle and this means that the internal diffusion phase Only that controls the adsorption process.

Table. 6 Results of chromium(III) adsorption after 24 h at concentrations of (600-800-1000-1500-2000-2500-3000)ppm

Ce (SB-KOH) (mg/l)	Ce (SB-N) (mg/l)	Co (mg/l)
244	387	600
324	505	800
404	588	1000
603	857	1500
788	1141	2000
804	1414	2500
1055	1644	3000

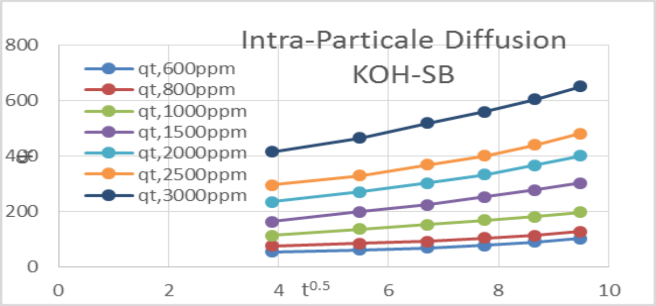
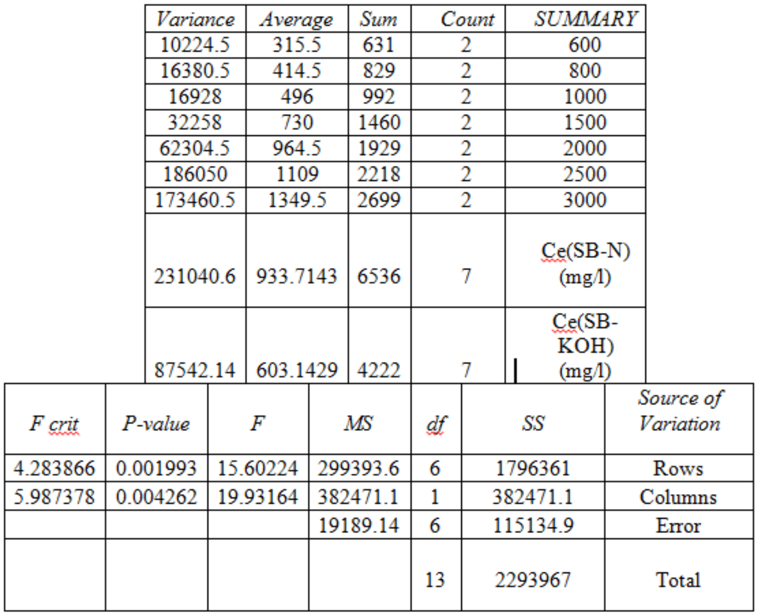


Figure 3 Curve of the internal diffusion equation at (600-800-1000-1500-2000-2500-3000) ppm

Table. 7 shows ANOVA Two-Factor for the results of treating the industrial water containing the ion (Cr^{3+}), a variation in the efficacy of the treatment, whether when the concentration of the chromium ion changed (from 600 to 3000 ppm) or the material used in the treatment changed (SB-N or SB-KOH), and KOH-SB outperformed N-SB at all conditions.

Table. 7 ANOVA Two-Factor for the results of treating the industrial water containing the ion (Cr^{3+})



Variance	*Average*	*Sum*	*Count*	*SUMMARY*
10224.5	315.5	631	2	600
16380.5	414.5	829	2	800
16928	496	992	2	1000
32258	730	1460	2	1500
62304.5	964.5	1929	2	2000
186050	1109	2218	2	2500
173460.5	1349.5	2699	2	3000
231040.6	933.7143	6536	7	Ce(SB-N) (mg/l)
87542.14	603.1429	4222	7	Ce(SB-KOH) (mg/l)

F crit	*P-value*	*F*	*MS*	*df*	*SS*	*Source of Variation*
4.283866	0.001993	15.60224	299393.6	6	1796361	Rows
5.987378	0.004262	19.93164	382471.1	1	382471.1	Columns
			19189.14	6	115134.9	Error
				13	2293967	Total

Figure 4 shows the presence of two linear regions in the graphical line expressing the internal diffusion equation for the concentration of 2500ppm, as well as for all graphical lines at all concentrations, and it indicates the passage of the adsorption process in two stages. At the beginning of the adsorption process the adsorption is fast (Instantaneous) It occurs by diffusion of chromium (III) across the boundary layer of the adsorbent, followed by a second linear region representing the phase of diffusion inside the pores (i.e. gradual adsorption) which is dominant, especially at the end of the adsorption process where the diffusion of chromium (III) becomes slow due to a low concentration in the solution. The second stage in the drawn graphs, which represents the state of equilibrium, and forms the above, it can be said that the adsorption of chromium (III) on the surface of SB-KOH is governed by the two stages of the external mass transfer (boundary layer diffusion) and the internal diffusion stage within the pores of the adsorbent .[19]

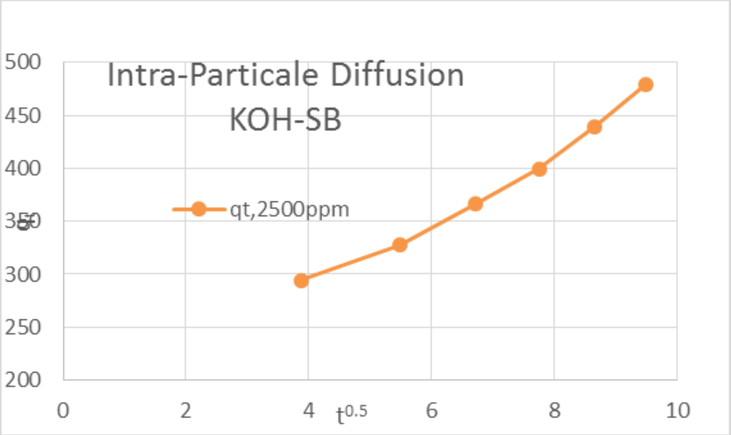


Figure 4 Curve of the internal diffusion equation at 2500ppm

Table 5 shows a comparison of the results of the optimal engineering theoretical study that we obtained for the binding of chromium with alginates, as the values we obtained are less than the values found in similar studies [20] and thus the Cr^{3+} - alginate binding is done by forming complexes.

Table 5 Mean chromium-oxygen distances, Cr - O

Mineral or compound	Cr - O, Å
This study	1.22 (COO^-)
This study	1.74 (OH)
Synthetic knorringite $Mg_3Cr_2Si_3O_{12}$	1.958
Cr alum $KCr(SO_4)_{2}{\cdot}_{12}H_{2O}$	1.961
Synthetic Cr_2O_3 eskolaite	1.986
Synthetic uvarovite $Ca_3Cr_2Si_3O_{12}$	1.994
Synthetic $YCrO_3$ perovskite	1.984
Synthetic $LiCrSi_2O_6$ pyroxene	1.992

From Fig. 5, we note that the Cr^{3+}-alginate bond cannot be electrostatically linked, because of the bond length forming the complex is smaller than the sum of the two diameters Cr^{3+} and O^{2-}

r (Cr^{3+}) = 65 pm [21] , r (O^{2-}) = 139 pm[22] , r (Cr^{3+}) + r (O^{2-}) = 204 pm

This explains the results of Freundlich and Langmuir and the increase in the maximum adsorption capacity q_m and the proportion of chromium (III) retention at high concentrations and forms a strong bond that works to retain chromium (III) in sugarcane bagasse and thus form complexes between chromium(III) and alginate (COO^-, O^{2-})

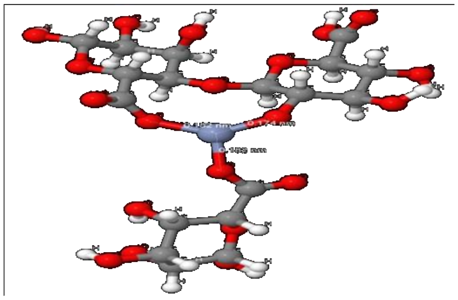


Figure 5 DTT/B3LYP optimized geometry of chromium (III) with sugarcane bagasse.

The obtained theoretical and practical results were confirmed studying the Temkin isometric model as in Table 6, where the interaction between the adsorbent material and the active sites of the adsorbent was explained the nature of the adsorption between the chromium (III) and the sugarcane bagasse through b = -ΔH was determined and the type of adsorption was chemically matched the Temkin's calculated results using solver package..

Table 6 Isotherm parameters obtained using the Temkin method for chromium (III) adsorption on SB –N, SB- KOH

Temkin	$b=-\Delta H_{20°C}$ (J/mol)	K_T
KOH-SB	4.5	0.0048
N-SB	6.38	0.003

$b=-\Delta H_{20}$°C : Represents the variation in adsorption energy (J / mol).

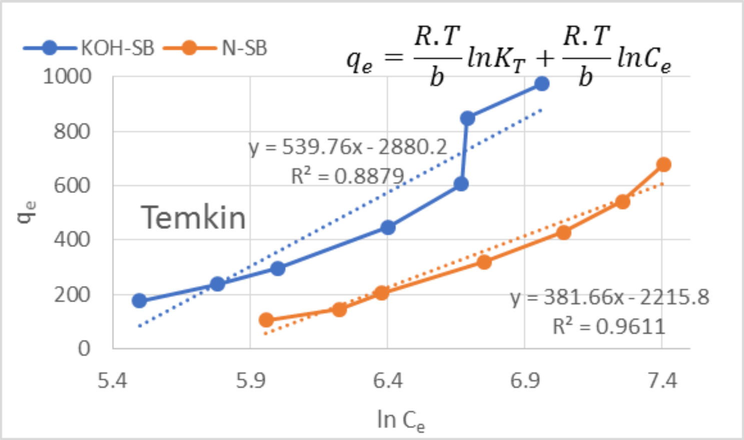


Figure 6 Isotherm parameters the Temkin method for chromium (III) adsorption on SB –N, SB- KOH.

Conclusion

Based on the findings of the study, Langmuir show within the studied concentrations of chromium (III) adsorption, and the studied adsorption does not apply. Isometric of Freundlich shows that the adsorption process occurs on heterogeneous surfaces and with an exponential distribution of the active sites and their energies, and indicates the heterogeneity of the relative energy distribution within the adsorption sites. ANOVA Two-Factor shows for the results of treating the industrial water containing the ion (Cr^{3+}) a variation in the efficacy of the treatment, whether when the concentration of the chromium ion changed (from 600 to 3000 ppm) or the material used in the treatment changed (SB-N or SB-KOH), and KOH-SB outperformed N-SB at all conditions. The internal diffusion equation showed that the absorption of chromium (III) on the SB-KOH surface is governed by two phases of the outer mass transfer (boundary layer diffusion) and the internal diffusion phase within the pores of the absorbent. The theoretical study showed the mechanism of chromium (III) binding with alginate Cr^{3+}-alginate bond cannot be electrostatically linked, because the bond length in the formed complex is smaller than the sum of the two diameters Cr^{3+} and O^{2-}. This explains the results of Freundlich and Langmuir and the increase in the maximum adsorption capacity q_m and the proportion of chromium(III) retention at high concentrations and forms a strong bond that works to retain chromium (III) in sugarcane bagasse and thus form complexes between chromium(III) and alginate (COO^-, O^{2-}). The obtained theoretical and practical results confirming the Temkin isometric model study, where the interaction between the adsorbent material and the active sites of the adsorbent was explained the nature of the adsorption between the chromium (III) and the sugarcane bagasse through $b = -\Delta H$ was determined as Temkin's calculated results matched the computed results using solver.

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