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Modification Of The Granular Activated Carbon And Its Effect On Removal Of Cr(VI) From Aqueous Solution In Batch And Fixed-Bed Systems

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Abstract:

The adsorption processes of Cr(VI) from aqueous solution onto a granular activated carbon (GAC) and a modified granular activated carbon (MGAC) with $AgNNO_3$*,* $FeCL_3$ *and* Na_2EDTA *have been investigated. The surface characteristics of these activated carbons were measured. The results showed that the MGAC has a lower surface area and more active functional groups compared with the GAC. Adsorption parameters such as adsorbent dosage, pH of solution, temperature and contact time of the adsorption onto GAC and MGAC have been investigated in a batch adsorption experiments in order to obtain the optimum conditions for the Cr(VI) adsorption process. Thermodynamic modeling using temperatures studies was done to reveal the nature of adsorption which indicated that the process was spontaneous and physical in nature. Experimental equilibrium data have been obtained and correlated with Langmuir and Freundlich isotherms for the determination of the adsorption potential. The results have shown that the Langmuir isotherm model better fits the experimental data compared with the Freundlich isotherm for both GAC and MGAC. It was found that the MGAC has a higher Cr(VI) adsorption capacity* (q_m)*, with 11.082, 14.214, 25.842, 25.842 mg/g for GAC,* (Ag^{+1}*-GAC),* (Na^{+1}*-GAC) and* (Fe^{+3}*-GAC) respectively. The breakthrough curves for the adsorption column test was obtained in a continuous adsorption fixed-bed experiment, The measured breakthrough times for GAC,* (Ag^{+1}*-GAC),* (Na^{+1}*-GAC) and* (Fe^{+3}*-GAC) were found to be 10, 30, 40 and 60 min, respectively.*

Keywords: Adsorption, GAC, MGAC, Cr (VI), FTIR, Batch system, Fixed-bed system.

تطوير الكاربون المنشط الحبيبي وتأثير ذلك على إزالة الكروم السداسي من المحلول الملوث باستخدام أنظمة الدفعة الواحدة والمستمرة

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الخلاصة :

تناول هذا البحث عملية الامتزاز للكروم السداسي باستخدام الكاربون المنشط الحبيبي والكاربون المنشط الحبيبي المعامل كيماويا باستخدام Na_2EDTA, $FeCL_3$, $AgNNO_3$. تم قياس الخواص السطحية لأنواع الكاربون المنشط بنوعية الاعتيادي والمطور. بينت النتائج أن الكاربون المنشط الحبيبي المطور (MGAC) يمتلك مساحة سطحية أقل ومجاميع فعاله أكثر نشاطاَ. محددات الامتزاز مثل جرع المادة المازه، درجة حموضة السائل، درجة الحرارة و وقت التلامس باستخدام (GAC) و (MGAC) تم دراستها بتجارب الامتزاز ذو الدفعة الواحدة للحصول على أفضل الظروف لعملية امتزاز الكروم السداسي. موديل الثرموداينمك باستخدام تجارب درجة الحرارة تم إنجازها لإيجاد وتحديد نوعية عملية الامتزاز فوجد أنها من نوع التفاعلات التلقائية والفيزيائية بطبيعتها. بيانات تجارب التوازن تم أيجادها وتم ربطها باستخدام موديلات لآنكَمير وفريندلج. النتائج أظهرت أن موديل لآنكَمير يحقق أفضل توافق مع النتائج العملية بالمقارنة مع موديل فريندلج لكلا النوعين، الكاربون المنشط الحبيبي والمطور. وتم استنتاج أن الكاربون المنشط الحبيبي المطور يمتلك سعه امتزاز أكبر للكروم السداسي وكالتالي: 11.082, 14.214, 25.842, 35.461 ملغم/غم لكل من GAC، Ag^{+1}-GAC، Na^{+1}-GAC، Fe^{+3}-GAC على التوالي. تم الحصول على منحنيات الانكسار من التجارب ذات النمط المستمر على عمود الامتزاز الثابت. تم إيجاد أوقات الانكسار المقاسة لكل من GAC، Ag^{+1}-GAC، Na^{+1}-GAC، Fe^{+3}-GAC لتكون 10، 30، 40، 60 دقيقة على التوالي.

كلمات دالة : الامتزاز، الكاربون المنشط الحبيبي، الكاربون المنشط الحبيبي المطور، الكروم السداسي، نظام الدفعة المتقطعة، نظام الدفعة المستمرة.

1. Introduction

Water pollution by chromium is due to both, natural sources and manmade activities. Chromium is found in rocks, animals, plants, soils and in volcanic dusts and gases [1]. With the rapid development of the galvanization industry in the world, the amount of hexavalent chromium Cr(VI) containing wastewater generated by the industry has increased dramatically. Due to its high solubility and toxicity to living organisms, Cr(VI) containing wastewater has been classified as a top-priority toxic pollutant by the united state environmental protection agency (USEPA), as well as the world health organization (WHO). Furthermore, Cr(VI) is highly mobile in soil and aquatic system, and also is a strong oxidant capable of being adsorbed by the skin[2]. Considering its toxic and carcinogenic nature, the maximum levels permitted for trivalent chromium in wastewater and potable water are 5 mg/L and 0.05 mg/L respectively[3].

Various methods have been used for treating wastewater containing Cr(VI), including electro-chemical precipitation[4], ion exchange[5], membrane ultrafiltration[6], and reverse osmosis[7]. The adsorption method is widely used for wastewater treatment because of its convenient operation, its effectiveness and relatively low cost[8]. Activated carbon is the main adsorbent material used in the adsorption process because of its high specific surface area, which is normally in the range of 1000–1500 m^2/g[9]. It has also been used as an adsorbent to remove Cr(VI) from aqueous solutions [10].

However, high cost of activated carbon encourages using the low cost and/or waste materials as adsorbent for various pollutant removals from aqueous environment[11]. It has been reported that surface modification with suitable chemicals and impregnation techniques not only increase adsorption capacity but also add selectivity to carbon[12].

The main objective of this paper was to correlate the adsorption performance of modified activated carbon with the unmodified activated carbon. Moreover the work was carried out to develop a cost effective process for Cr (VI) adsorption from their aqueous solutions.

2. Materials and methods

2.1 Chemicals and Adsorbent

All the chemicals used in this study were of analytical grade and were obtained from Sigma-Aldrich.Com, UK. Granular Activated Carbon (GAC) was also obtained from the same company. The Cr(VI) stock solution was prepared by dissolving 2.829 g $K_2Cr_2O_7$ dried at 378K for 2 h in a 1000 ml volumetric flask with deionized water to form a Cr(VI) stock solution with a concentration of 1000 mg/L.

2.2 Preparation and Characterization of modified GAC

The GAC was washed several times with distilled water and dried in hot air oven at 383K for 2 hours to remove moisture completely, cooled to room temperature and stored in polybags. 50 grams of the dried material was treated with 120 ml of ferric chloride solution $FeCl_3$, sodium ethylene diamine tetra acetic acid Na_2 EDTA and sliver nitrate $AgNo_3$ containing 2.5% of Fe^{3+}, Na^{+1} and Ag^{+1} respectively[13]. The pH of the solution was raised to 12 by the addition of 1N NaOH solution. High pH value for impregnation was considered for generation of maximum surface charges on the surface of GAC impregnated with Fe^{3+} (GAC-Fe^{3+}), Na^{+1}(GAC-Na^{+1}) and Ag^{+1}(GAC-Ag^{+1}). The impregnation was carried out at 343K on a water bath till the complete evaporation of water was observed and then it was dried at 383K for 24 h. The dried material was washed with Millipore water till the washing liquid became free from residuals iron as sodium and silver and then dried to constant weight. The Brunaur, Emmett and Teller surface area (BET) and total pore volume of the adsorbent was calculated by physisorption surface analysis on surface area analyzer, model micrometrics chemisorb 2720. Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 6700, USA) was employed to determine the type of functional groups present on adsorbent's surface before and after modification.

2.3 Batch Experiments

Batch experiments for optimization of process parameters were carried out in 250 ml round bottom flasks with working volume of 100 ml at 150 rpm in an incubator cum orbital shaker (Heidolph, No.549-59000-0-0, Germany). All the experiments were carried out in triplicates and average results were used. The range of various process parameters was varied as adsorbent dose: 0.1-1.2 g, contact time: 30-360 min, pH: 2-6, temperature: 293K- 333K and initial concentration of 50 mg/L. The suspensions were centrifuged and the supernatant was then analyzed by a standard spectrophotometric method using a spectrophotometer (Shemadzu, model UV-160 A) at the maximum wave absorbance of 540 nm. The percentage of adsorption *E* and the adsorption capacity q_e were calculated as:

$$E = \frac{C_o - C_{eq}}{C_o} \times 100\% \qquad (1)$$

$$q_e = \frac{V_L (C_o - C_{eq})}{M} \times 100\% \qquad (2)$$

Here C_o and C_{eq} are the initial and equilibrium concentrations of Cr(VI) in mg/L, respectively, V_L is the volume of solution in liter and *M* is the mass of adsorbent in g.

2.4 Continuous adsorption Fixed- bed experiments

The fixed-bed breakthrough curve was measured by a continuous adsorption experiment. An acrylic column of (50 mm) inner diameter and (0.5 m) height was packed with 100 g GAC or MGAC as shown in **Figure.(1)**. There was a distributor on the top of the column in order to allow a homogeneous flow distribution. Porous organic plastic supports were used to hold the carbons in the column. Cr(VI) initial concentration solution of 50 mg/L was pumped through the carbon bed at the rate of 2.78×10^{-6} m^3/s using a peristaltic pump (BT-100, China). Effluent samples were taken at various times for Cr(VI) concentration analysis.

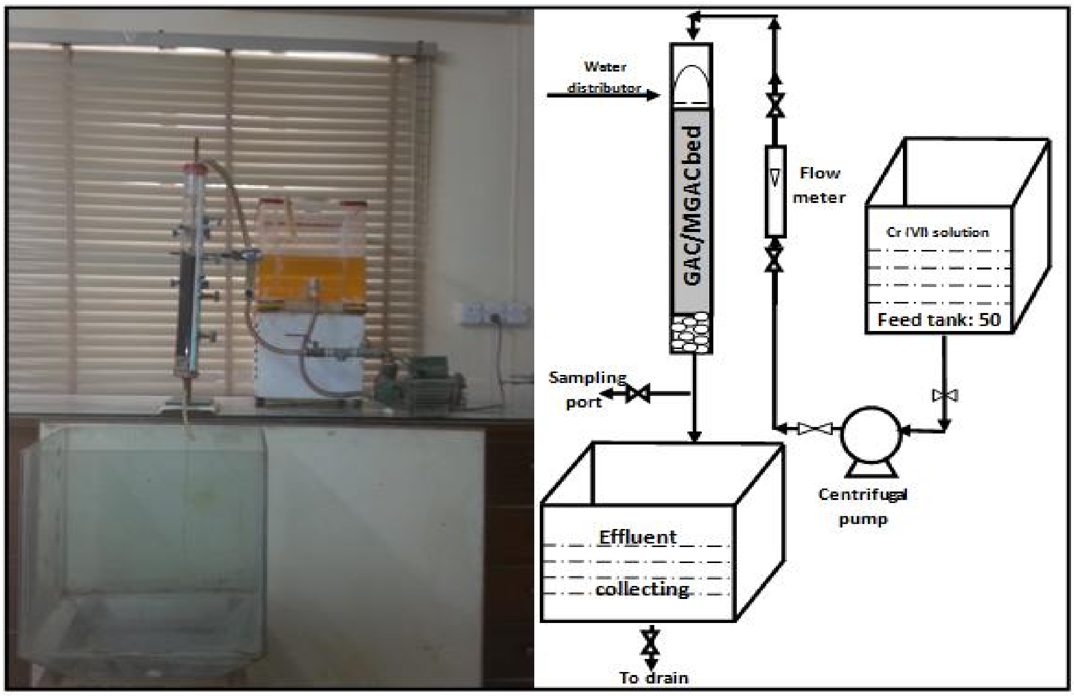

Fig.(1) Photo and Schematic diagram of the experimental set up for a continues process. process.

3. Results and Discussions

3.1 Surface Analysis

The basic characteristics of GAC and MGAC including particle size, surface area, pore volume and bulk density are measured at the laboratories of (Petroleum Development and Research Center, Baghdad) and listed in Table 1. As evident from the Table, surface area and pore volume of GAC decreases after modified with $FeCl_3$, Na_2EDTA and $AgNo_3$ solutions respectively indicating occupation of pores on the surface of GAC with Fe^{3+}, Na^{+1} and Ag^{+1} ions. Compared with the surface area of 610 m^2/g for the GAC, the surface area of the MGAC has decreased to be 380, 420 and 560 m^2/g for (Fe^{+3}-GAC), (Na^{+1}-GAC) and (Ag^{+1}-GAC) respectively. The decrease in the surface area as mentioned above is mainly due to the decrease in the micropore volume resulting from pore blockage by the surface oxide groups existing in some of the micropores. However, the bulk density increased due to the increased weight of adsorbents. Similar results have been reported by Liu etal., 2005 **[14]**. Thus, it is expected that (Fe^{+3}-GAC) will have more affinity to adsorb Cr(VI) compared with other types of granular activated carbon.

Table 1 General Characteristics of GAC and MGAC.

Parameter	GAC	Fe^{+3}-GAC	Na^{+1}-GAC	Ag^{+1}-GAC
Particle Size, mm	0.6	0.6	0.6	0.6
Bulk Density, kg/m^3	650	740	690	674
Surface Area, m^2/g	610	380	420	560
Total pore Volume, m^3/g	0.213	0.032	0.102	0.176

3.2 Fourier Transform Infrared Spectroscopy (FTIR) Studies

FTIR spectra of GAC and MGAC are shown in Figure 2. The spectra of the GAC and MGAC samples were recorded between 4000 and 1000 cm^{-1} using a Nicolet 6700 FTIR. Table 2 shows the main functional groups responsible for adsorption of chromium ion before and after GAC modification. The results indicate that the bands groups shifted to lower frequency (Transmission, T %). The bands of functional groups shifted to lower frequency with a total amount of 17, 25.2, and 31.7% for Ag^{+1}-GAC, Na^{+1}-GAC and Fe^{+3}-GAC respectively. Therefore, the order of adsorption of Cr(VI) by GAC and MGAC will follow the sequence: (Fe^{+3}-GAC) > (Na^{+1}-GAC) > (Ag^{+1}-GAC). The main functional groups proposed for the Cr(VI) are carboxylic, amino, alkane and others. Huang et al., 2009[15] studied the adsorption processes of Cr(VI) from aqueous solution onto a granular activated carbon (GAC) and modified activated carbon (MAC) with nitric acid. They found that, the modified activated carbon appears to have more pronounced peaks for the MAC than GAC appearing at 1610, 1240 cm^{-1} are ascribed to the formation of, or to an increase in, the already available oxygen functionalities (highly conjugated C=O stretching, C–O stretching in carboxylic groups, and carboxylate moieties). These results also indicate that HNO_3 treatment gave rise to a greater increase in C=O phenol bonds in carboxylic acid and lactone groups[15].

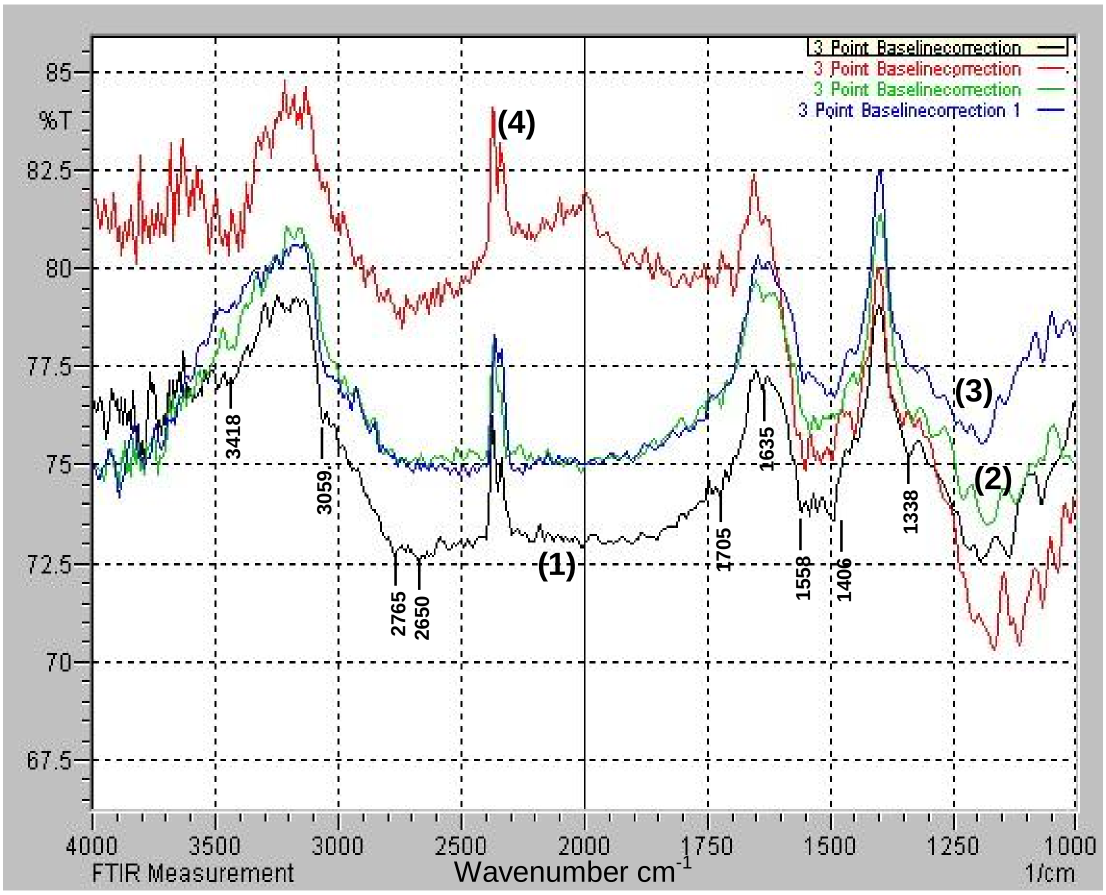

Fig.(2) FTIR spectra of GAC (1) before, (2) after Ag^{+1}-GAC, (3) after Na^{+1}-GAC and (4) after Fe^{+3}-GAC modification.

Table(2) Functional groups for GAC and MGAC.

Wave number, cm^{-1}	Type of bond	Functional group	T (%) GAC	T (%) Ag^{+1}-GAC	T (%) Na^{+1}-GAC	T (%) Fe^{+3}-GAC
3418	$-OH^-$	Carboxylic acid, Amide, Amine	77	77.3	79	80.5
3059	$-OH^-$	Carboxylic acid	76	78	78	82
2765	$-OH^-$	Carboxylic acid	73	75	75	77.5
2650	$-CH^+$	Alkane	72.7	77	77	77
1705	-C=O	Carboxylic acid	74	76	77	79
1635	$-CH^+$	Alkane	77	78	80	82
1558	$-OH^-$	Carboxylic acid	73.7	76	77	75
1406	$-OH^-$	Carboxylic acid	73.5	76	77	75
1338	$-OH^-$	Carboxylic acid	75.4	76	77.5	76
Summation of T, %			672.3	689.3	697.5	704
Difference in T, % after modification				17	25.2	31.7

3.3 Effect of the adsorbents dosage

The effect of the GAC and MGAC dosage on the adsorption was investigated in the range of 0.1–1.2 g, while the initial concentration, contact time, pH value and temperature of the Cr(VI) solution were fixed at 50 mg/L, 6 h, pH 5, and Temp.303K respectively. The result is shown in Fig. 3. which shows that, the percentage of adsorption generally increased with an increase in the GAC and MGAC up to a certain value, and then remained constant above a dosage of 1.1, 0.9, 0.8, and 0.6 g for GAC, (Ag^{+1}-GAC), (Na^{+1}-GAC) and (Fe^{+3}-GAC) respectively.

This indicates that the surface modification of the GAC with the three chemical solutions significantly improved the Cr(VI) removal capacity compared with the GAC with an optimum dose of 1.1, 0.9, 0.8 and 0.6 for GAC, (Ag^{+1}-GAC), (Na^{+1}-GAC) and (Fe^{+3}-GAC) respectively. Removal efficiency increases from 21.13 to 62.37 % onto GAC as the mass increases from 0.1 g to 1.1 g, 24.08 to 68.42 % as the mass increases from 0.1 to 0.9 g onto (Ag^{+1}-GAC), 34.08 to 76.58 % onto (Na^{+1}-GAC) as the mass increases from 0.1 g to 0.8 g and from 38.086 to 94.072% onto (Fe^{+3}-GAC) as the mass increases from 0.1 g to 0.6 g. It is clearly seen that, the removal efficiency increases as the adsorbent mass increases. With increasing adsorbent dosage more surface area is available for adsorption. As the adsorbent mass increases the number of binding sites for the ions also increases. After some point, sorption capacity was steady due to a screen effect between adsorbent, this produced a block of the adsorbent active sites by an increase of chromium ions in the system. This results agreed with that obtained by Ahmed, 2013 [16]. Therefore, The dose at which maximum Cr(VI) removal was observed is considered as the optimum dose for further study.

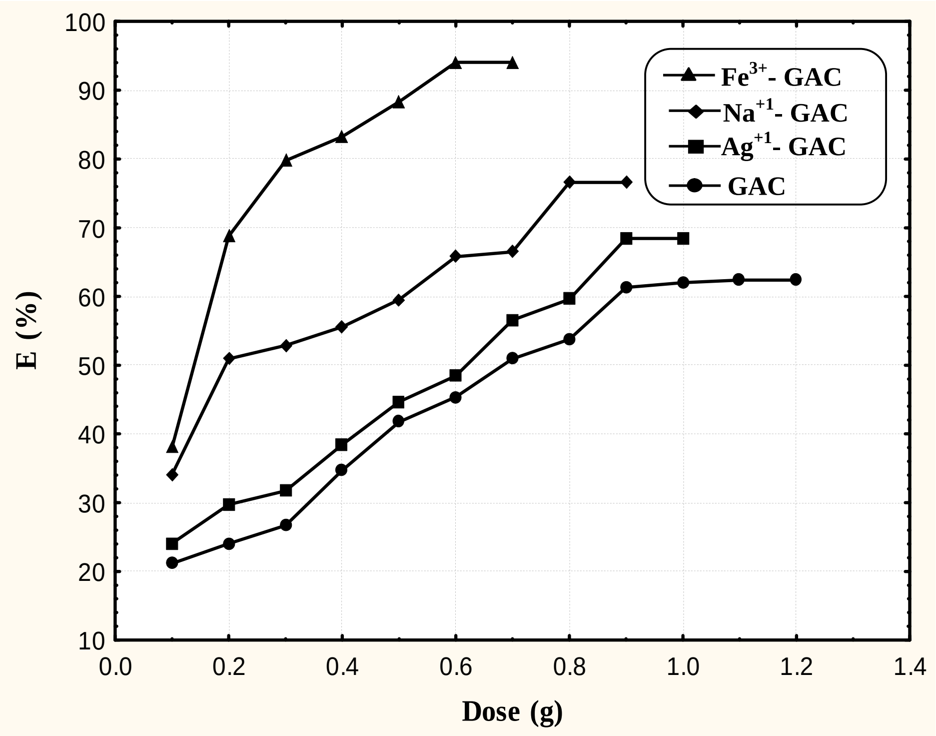

Fig. (3) Effect of GAC or MGAC dose on percentage adsorption (pH=5, C_o= 50 mg/L, contact time=6 h and temperature= 303 K).

3.4 Effect of pH

Because Cr (VI) ions in aqueous solutions starts precipitating at pH > 6[17], the effect of the solution pH on the adsorption behavior was investigated in the range 2.0–6.0, while the initial concentration, contact time and temperature were fixed at 50 mg/L, 6 h and 303 K. The results are shown in **Figure.(4)**. Fig. The chromium adsorption onto the GAC and MGAC is strongly pH dependent. The percentage of adsorption increases at lowe pH values from 2.0 to 5.0 for MAC. Then above pH of 5.0, the percentage of adsorption began to decrease. This results suggest that the optimal pH of solution for adsorption of Cr(VI) should not exceed a value of 5.0 below the precipitation pH (6). At a very low pH the metal uptake was less and this is due to the fact that activated carbon surfaces are closely associated to H_3O^+ and access of metal ions to adsorbate walls would be restricted as a result of repulsive forces. Metal uptake were increased with pH variation from 3 to 5, this is due to more ligands with negative charge being exposed with the subsequent increase in attraction sites to positively charged metal ions. On the other hand, at a high values of pH (above 5), adsorption of the Cr(VI) ions decreased probably because of the metal precipitation as hydroxides which depend on the pH and the ion concentration. Similar results has been found by Z. Al-Qodah, 2006[18].

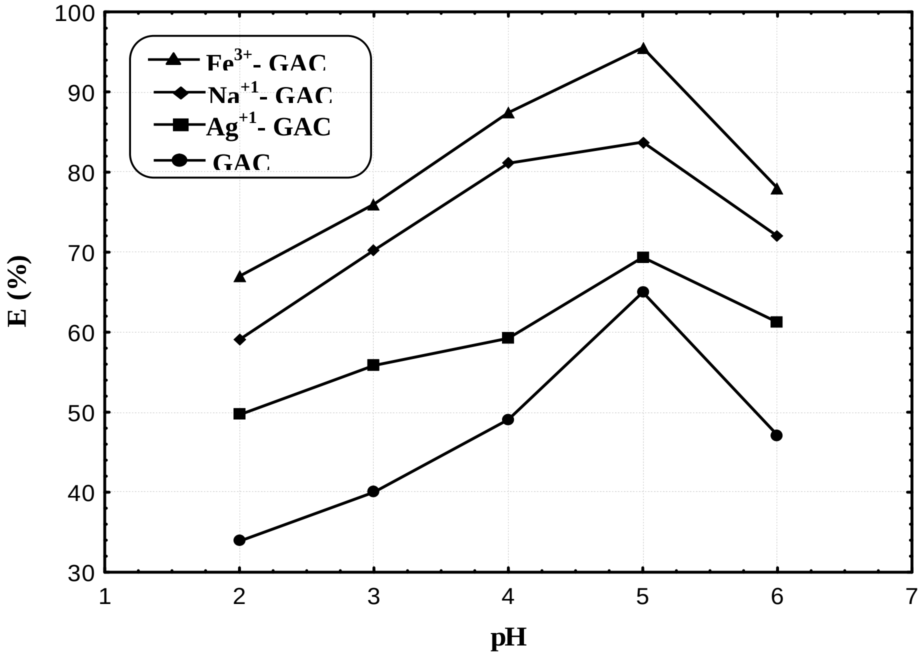

Fig. (4) Effect of pH on percentage adsorption (C_o= 50 mg/L, contact time=6 hr and Temp.= 303K).

3.5 Effect of the temperature and the thermodynamic constants

Temperature is an important parameter in the context of adsorption on solid phase. In the present case the effect of temperature on the extent of solute adsorption was investigated in the range from 293-333 K. The results is shown in **Figure.(5)**. As a whole, it is clearly obvious that as the temperature increases the percentage removal at the same initial adsorbate concentration decreases. This means that the rate of desorption was more significant than the rate of adsorption, which implies that adsorption is an exothermic reaction, a well-known scientific fact[19]. For this reason a temperature of 293K was applied in all further adsorption experiments.

It is well known in the consideration of the thermodynamics of adsorption process

that the temperature has an indispensable effect on adsorption of metal ions. The wide range of temperature variation causes a change in thermodynamic parameters like ΔG^o, ΔH^o and ΔS^o. The evaluation of these parameters facilitates the choice of the adsorption mechanism approach. The data of removal percent due to changing temperature led to the finding of these parameters. The standard Gibbs free energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) of the adsorption process can be measured from the following equations[20, 21]:

$$\Delta G^o = -RT \ln Kc \tag{3}$$

where K_C is the equilibrium constant, R is the universal gas constant= 0.8314 kJ/mol.K and T is the temperature in K.

$$K_C = \frac{C_o - C_{eq}}{C_{eq}} \quad (4)$$

Also, enthalpy changes (ΔH) and entropy changes (ΔS) can be estimated by the following equation:

$$\Delta G^o = \Delta H^o - \Delta S^o T \quad (5)$$

The free energy (ΔG^o) variation indicates the degree of spontaneity of adsorption and the higher negative value reflects a more energetic favorable adsorption[22]. Figure 6 shows the thermodynamic constants of adsorption for Cr(VI) onto GAC and MGAC. The value of enthalpy ΔH° was -3.694, -4.090, -4.656, and -6.485 kJ/mol for Cr(VI) onto GAC, (Ag^{+1}-GAC), (Na^{+1}-GAC) and (Fe^{+3}-GAC) respectively, suggested the physisorption and exothermic nature of adsorption. This is also supported by the decrease in the values of percentage adsorption of adsorbents with the rise in temperature[23]. The values of entropy ΔS°, −0.012, −0.013, -0.014 and −0.019 J/mol K, reflect the affinity of Cr(VI) ions to be adsorbed onto GAC, (Ag^{+1}-GAC), (Na^{+1}-GAC) and (Fe^{+3}-GAC) respectively. As shown from Fig. 6, the value of the free energy ΔG° increase with the increase in temperature indicates that the adsorption process is exothermic, and it is thereby favored with decrease in temperature, thus, the process is better carried out at low temperature[24].

It should be noted that ΔG values up to (20 kJ/mol) are consistent with electrostatic interaction between adsorption sites and the metal ion (physical adsorption). While ΔG values are more negative than (40 kJ/mol), then charge sharing or transfer from the adsorbent surface to the metal ion to form a coordinate bond could take place (chemical adsorption)[25]. The obtained ΔG values from this study for all adsorbents was less than 20 kJ/mole as shown from **Figure.(6)**, hence the physical adsorption has been predominated in the adsorption of Cr (VI) ions on GAC and MGAC.

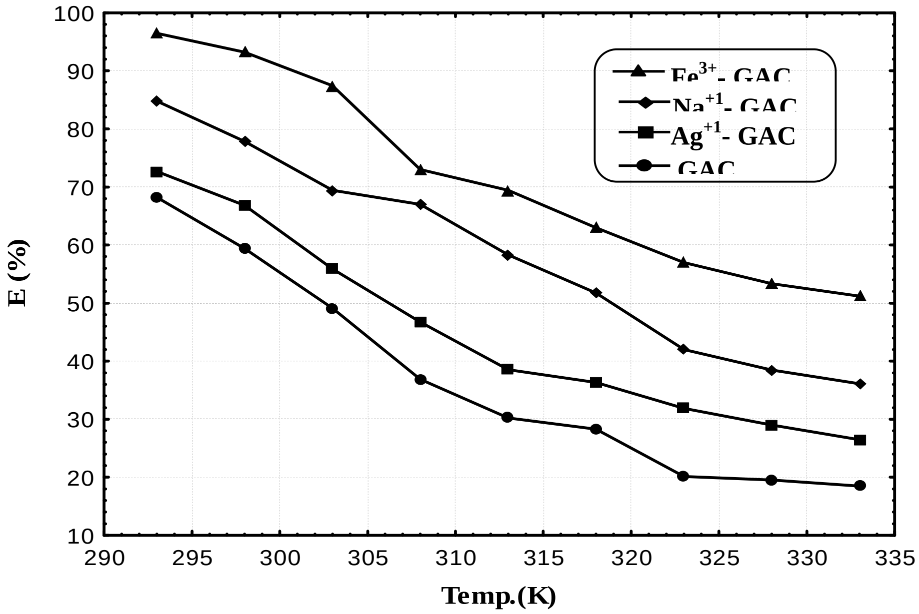

Fig. (5) Effect of temperature on percentage adsorption (C_o= 50 mg/L, pH=5, contact time=6h).

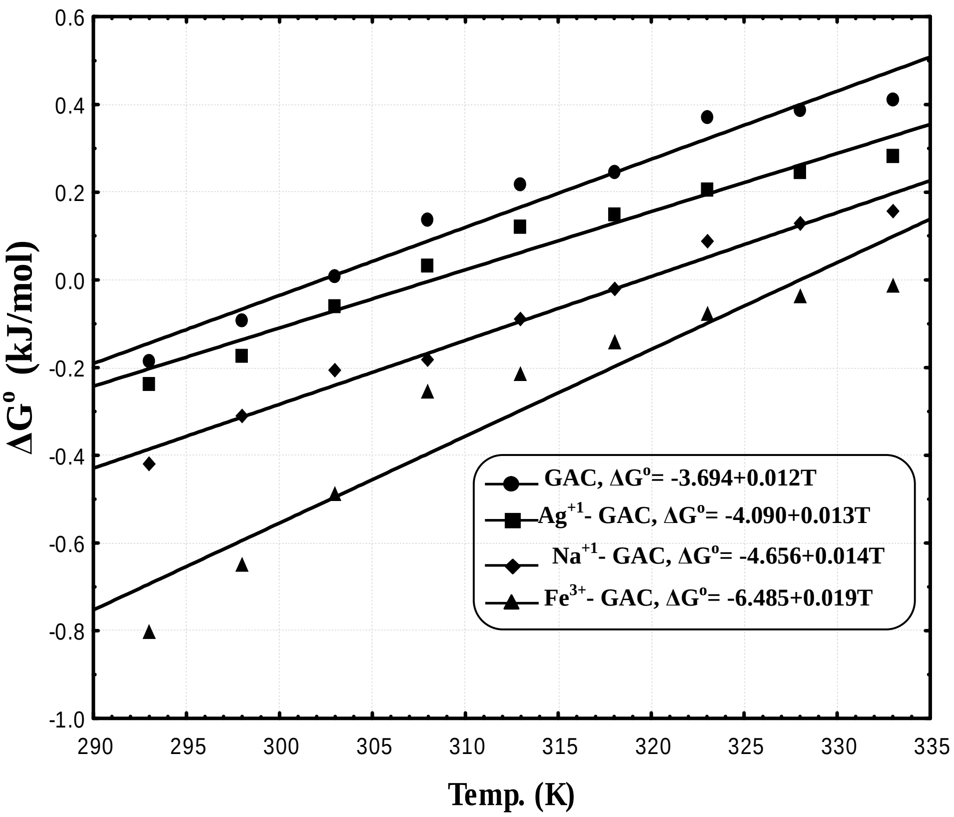

Fig. (6) Free energy change (ΔG°) for Cr (VI) adsorption onto GAC and MGAC.

3.6 Effect of the contact time

The effect of the contact time on the adsorption was investigated in the range from 30 to 360 min at optimum dosage, pH and temperature. The results are shown in **Figure.(7)**.

Sufficient contact time is needed for the adsorption process to reach equilibrium for the maximum Cr(VI) adsorption on GAC or MGAC. **Figure.(7)** indicated that the equilibrium time for Cr(VI) adsorption on GAC and MGAC is about 330, 300, 240 and 210 min, respectively. The equilibrium results also indicated that the surface modified (Fe^{3+}-GAC) can remove Cr(VI) more effectively from the solution compared with untreated GAC and with Ag^{+1}-GAC, Na^{+1}-GAC. Hence 210 min appears to be the optimum contact time for Fe^{3+}-GAC. Ghosh, 2009 pretreated fresh activated carbon (AC) by heating with mineral acids (sulfuric acid and nitric acid) at high temperature. The results showed that, removal of Cr(VI) by acid modified adsorbents was almost ceased within 6 h (360 min) of agitation period, whereas it took 8 h (480 min) by AC[26].

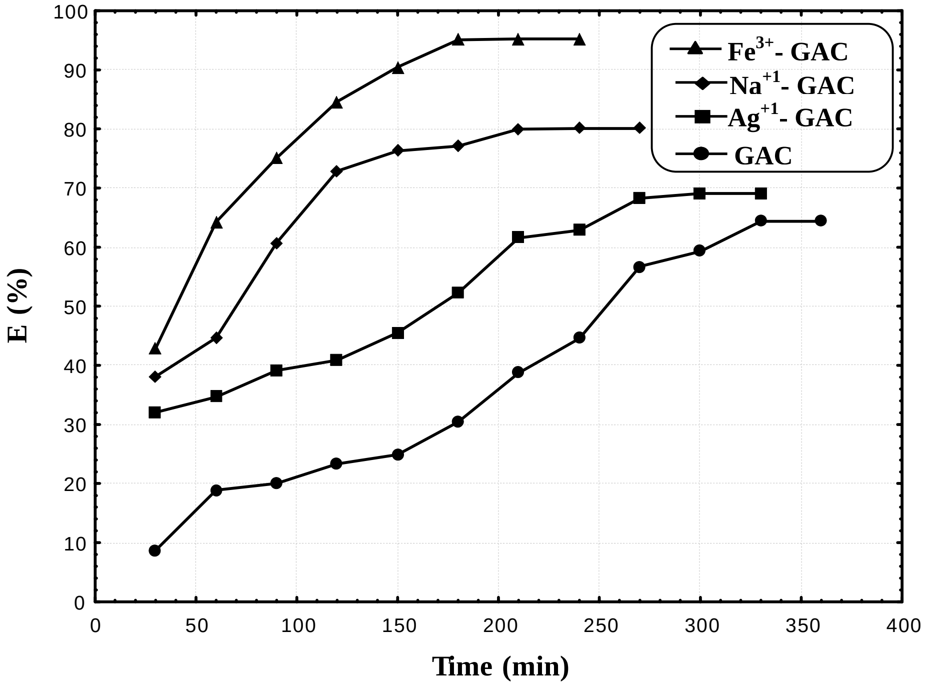

Fig. (7) Effect of contact time on percentage adsorption (pH=5, C_o= 50 mg/L, and temperature= 293K).

3.7 Adsorption isotherm models

In order to determine the adsorption potential, an adsorption isotherm is essential. The experimental data for Cr(VI) onto GAC and MGAC obtained with an initial Cr(VI) concentration of 50 mg/L was correlated with the Langmuir and Freundlich isotherms. The Langmuir isotherm is expressed as[27]:

$$q_{eq} = \frac{q_{\max} bC_{eq}}{1+bC_{eq}} \tag{6}$$

The Freundlich isotherm is expressed as:

$$q_{eq} = K_F \, Ceq^{1/n} \tag{7}$$

Here q_e (mg/g) is the amount of adsorbed Cr(VI) per gram of GAC or MGAC and C_{eq} (mg/L) is the equilibrium concentration of Cr(VI) in the bulk of the solution. q_{max} (mg/g) is the maximum adsorption capacity and b (L/mg) is the Langmuir equilibrium constant related to affinity between adsorbent and adsorbate. For the Freundlich model, K_F (mg/g)(L/mg)$^{1/n}$ is the constant related to adsorption capacity of the adsorbent and n is the exponent related to adsorption intensity. The adsorption isotherm for Cr(VI) onto GAC and MGAC is shown in **Figure.(8)**. The parameters for each model obtained from nonlinear statistical fit of the equation to the experimental data (Statistica, v6) are summarized in **Table 3.**

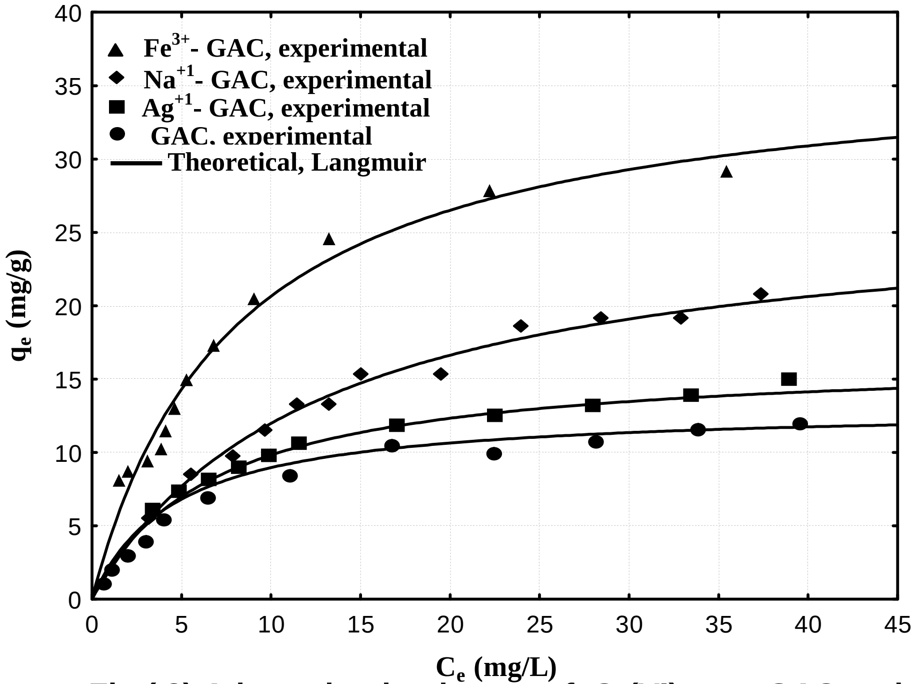

Fig.(8) Adsorption isotherms of Cr(VI) onto GAC and MGAC

Table 3 Langmuir and Freundlich isotherm constants.

Type of carbon	Langmuir isotherm			Freundlich isotherm		
	q_{max}	b	R^2	K_F	n	R^2
GAC	11.082	0.109	0.996	9.783	0.1000	0.957
Ag^{+1}-GAC	14.214	0.132	0.998	12.175	0.1683	0.969
Na^{+1}-GAC	25.842	0.145	0.997	16.043	0.9754	0.982
Fe^{3+}-GAC	35.461	0.217	0.992	27.033	1.3448	0.975

Table 3 shows that, the Langmuir isotherm model better fits the experimental data compared with the Freundlich isotherm for both GAC and MGAC. The maximum adsorption capacity (q_m) for Cr (IV) obtained from the Langmuir isotherm follow the sequence as: (Fe^{3+}-GAC) > (Na^{+1}-GAC) > (Ag^{+1}-GAC) > GAC. This means that Fe^{3+}-GAC has the highest affinity order for adsorbed Cr(VI), while ordinary GAC has the least affinity towards chromium ions.

The Langmuir isotherm is valid for monolayer sorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of sorption onto the surface and no transmigration of the sorbate over surface. The Langmuir model has been employed successfully in many real sorption processes. Satapathy and Natarajan, 2006 used Langmuir and Freundlich models to describe the adsorption of nickel ions using activated carbon modified with Potassium bromate. They found that, Langmuir model fit very well with the experimental data with determination coefficient R^2 of 0.9766 and 0.9927 for normal and modified activated carbon respectively[28].

3.8 Fixed-bed breakthrough curve

The fixed-bed breakthrough curve was obtained by a continuous adsorption experiment. The adsorption process was carried out according to the method described in Section 2.4. It can be seen from Fig. 9 that all Cr(VI) were initially retained in the fixed- bed because of full adsorption (no Cr(VI) in the effluent). With greater Cr(VI) solution flow through the bed, the Cr(VI) concentration in the effluent increases steadily until it reaches the same value as its inlet concentration (C_o), the so-called breakthrough point, when the fixed-bed is saturated. The measured breakthrough times for GAC and (Ag^{+1}-GAC), (Na^{+1}-GAC) are 10, 30, 40 and 60 min, respectively. These results proved that those obtained in batch system where (Fe^{3+}-GAC) is adsorbed Cr(VI) more strongly than other types of granular activated carbon.

The bed-depth service-time model is used to estimate the required bed depth for a given service-time. The BDST model can be expressed as below[29]:

$$t_b = \frac{N_o}{C_i u} Z - \frac{1}{C_i K} \ln\left(\frac{C_i}{C_b} - 1\right) \qquad (7)$$

where C_b is the solute concentration in the effluent of the column at breakthrough (at 10% breakthrough point , i.e. t_b at C_b=5 mg/L), C_i is the solute concentration in the effluent to the column (50 mg/L), N_o is the adsorption capacity, Z is the bed height (0.05 m), u is the superficial velocity (3.37×10^{-7} m/sec) and K is the rate constant which represents the solute transfer from the liquid phase to the solid phase. The parameters N_o and K for BDST model were obtained from nonlinear statistical fit of the equation to the experimental data (Statistica, v6) which are summarized in Table 4. The R^2 value mostly close to unity indicating the suitability of the BDST model to represent the adsorption of Cr(VI) in a fixed-bed of GAC and MGAC. The adsorption capacity N_o as shown in Table 4 for MGAC is higher than that for GAC. This result proved the results obtained in batch system for maximum adsorption capacity (q_m). This models has been used successfully by other researchers to estimate the required depth for a specific adsorption time[29, 30].

Table(4) parameters predicted from the BDST model for adsorption of Cr(VI) on GAC and MGAC.

Type of carbon	N_o, mg/L	K, L/mg.min	R^2
GAC	153.5	0.00022	0.981
Ag^{+1}-GAC	156	0.00045	0.992
Na^{+1}-GAC	164	0.00085	0.978
Fe^{3+}-GAC	190	0.00105	0.987

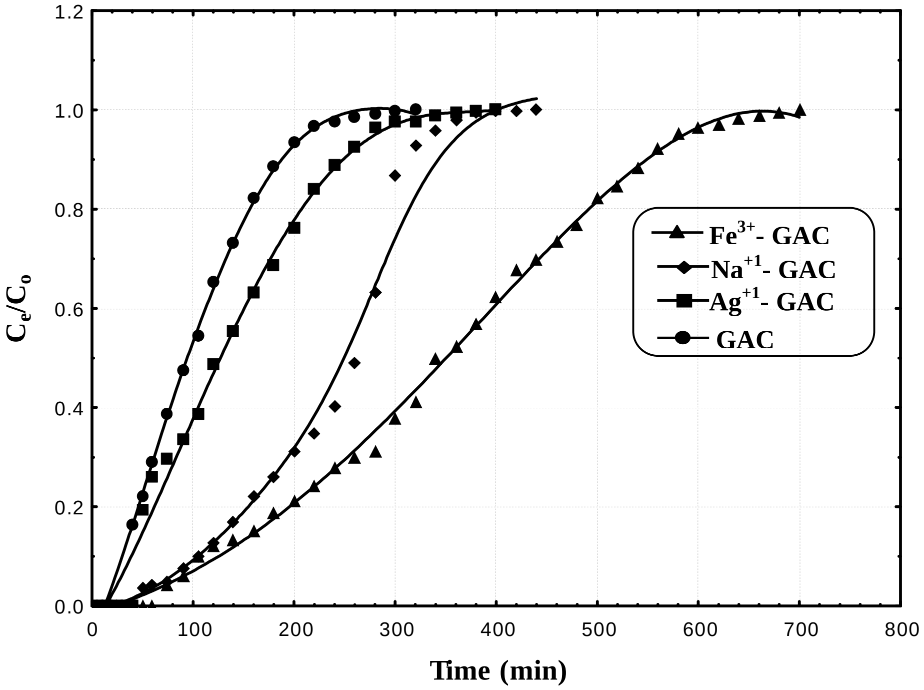

Fig. (9) Fixed- bed breakthrough curve for GAC and MGAC.

4. Conclusions

Adsorption using modified activated carbon case an increase in the removal efficiency of chromium ions from simulated wastewater, it's also decreases the contact time required for maximum adsorption. A decrease in optimum adsorbent dose required for maximum removal of chromium was also observed. Among the four grades of adsorbents, viz., GAC, (Ag^{+1}-GAC), (Na^{+1}-GAC) and (Fe^{+3}-GAC), Fe^{+3} modified granular activated carbon achieved significantly better degree and rate of removal of Cr(VI). $FeCl_3$-impregnated GAC reduced the adsorbent dosage from 1.1 g to 0.6 g , reduced the equilibrium time from 330 min to 210 min, and increased removal efficiency from 62.37 % to 94.072% and 64.35% to 95.23% for both cases respectively. Optimum pH and temperature were found to be 5 and 293K respectively.

Application of thermodynamic model to the data obtained by temperature studies revealed that adsorption of Cr(VI) on GAC and MGAC was spontaneous and physical in nature.

It was found that, the Langmuir isotherm model correlated the experimental data better than the Freundlich isotherm. Maximum adsorption capacity (q_{max}) of the GAC and MGAC calculated from Langmuir isotherm are 11.082, 14.214, 25.842 and 35.461 mg/g, for GAC, Ag^{+1}-GAC, Na^{+1}-GAC and Fe^{+3}-GAC respectively. Experimental data, after adsorption column study, fits well to linear form of BDST model. The equation can be modified to make suitable for a different flow rate and effluent Cr(VI) concentration.

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