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Efficiency of magnetic chitosan supported on graphene for removal of perchlorate ions from wastewater

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Abstract

In this study, we used a synthesized cross-linked magnetic chitosan with graphene oxide beads to study the removal of perchlorate from wastewater. The prepared complex was characterized using transmission electron microscopy (TEM), Fourier Transformation Infrared spectroscopy (FT-IR), vibrating sample magnetometry (VSM) and Thermal gravimetric analysis (TGA).

Several parameters were studied including the effect of pH, contact time and the co-existing anions. The study showed that the adsorption could be study in a wide range of pH. The study showed that the adsorption follows a pseudo-second order model and Langmuir adsorption isotherm. The enthalpy and negative Gibbs standard free energy showed that the adsorption process was exothermic and spontaneous. The perchlorate adsorbent can be regenerated well by 0.1% NaCl solution.
Keywords: magnetic chitosan, graphene, adsorption, kinetics, isotherm, perchlorate.

1. Introduction

Pollution is the main problem of the environment in the world which is the process of making parts of the environment (land, water and air) dirty and unsafe or unsuitable to use. This occurs through diffusion of pollutants into a natural environment [1]. The need to maintain a cleaner environment is the main subject of increasing concert to the environment list. There are many agents may cause pollutes such as heavy metals, dyes and anions [2-4].

Perchlorate ion (ClO$_4^-$) is an inorganic contaminant that its salts (mostly ammonium sodium and potassium are mainly used in production of different products like matches and telecoms tubes. Perchlorate affects human health and it was listed by USEPA 1998) and the guideline was close to 24.5 ppm [5].

Now the main challenge for environmentalists is removal of perchlorate from water especially perchlorate ion which is non-volatile and highly soluble in water [6]. There are many methods to remove perchlorate from drinking water such as adsorption, ion-exchange, biological remediation and different chemical catalytic reduction [7-10].
Adsorption is the most suitable one compared with other methods due to its advantages of high treatment efficiency, low cost and easy operation.

Graphene as adsorbent is also used to reduce perchlorate from water under some treatment like modification using cationic surfactant to enhance adsorption capacity. This always cost money and may lead to second pollution. For this reason, chitosan which is effective bio-adsorbent because it has good biodegradability and nontoxic and chemical resistance and mechanical properties [11-12].

Today, chitosan has been selected as an effective bio adsorbent for the reducing or recovery of toxic proteins, dyes and heavy metals due to many properties such as nontoxicity, good biodegradability, high chemical resistance and decent mechanical property [12-13].

In our study, chitosan was selected for different reason like it contains many amino (-NH$_2$) and hydroxyl (-OH) functional groups that are capable to interact with iron. Chitosan can also be changed easily by chemical or physical processes or through reaction with other polymers to synthesize chitosan derivatives or form new compounds [14-16]. Chitosan does not have hydrophobic properties. To increase it and increase adsorption capacity, some chemical modification is required [7].

It is obvious from literature that there are many studies on chemical modified chitosan. Wang, Y., Yan, T., Gao et al.[18] has prepared and applied magnetics hydroxypropyl chitosan/graphene oxide (MHCGO) composites to act as an adsorbent to decrease lead ion in aqueous solution. Heydaripour, J., Gazi et al. [19] synthesized very high porous with high surface area of some resin of magnetic and grafted chitosan to reduce the presence of 4-chlorophenol and phenol in aqueous solutions. Wang, Y., ShiL et al. [20] have prepared magnetic multiwall carbon nanotubes functionalized with hydroxy propyl chitosan as adsorbent of lead from water.

To avoid problems related to regeneration of chitosan, focusing on magnetic adsorbents in recent years was occurred. One of the most advantages of magnetic composites are high efficiency, very fast adsorption rate, and increasing the adsorption capacity [12, 20]. Magnetic properties for adsorbent always help in adsorption capacity and reducing filtration and centrifuging. [21].

Recently, many methods for using magnetically nanocomposit have been investigated. Omidvar, A., Jaleh et al [22] has studied the reduction of 4-nitrophenol (4-NP), Methyl Orange (MO), Methylene blue (MB) and Congo red (CR) by preparing GO/Fe$_3$O$_4$/Pd nanocomposite at room temperature. Wang, Y., et al [21] has Prepared magnetic hydroxyapatite-immobilized oxidized multi-walled carbon nanotubes (mHAP-oMWCNTs) as a good adsorbent for removal of Pb(II) and methylene blue (MB).
Oladipo, A et al. [23] prepared Chitosan-based magnetic nanobeads (CBN) and used for removal of boron from highly brackish wastewater.

The goal of this study is to remove perchlorate ions from wastewater, using magnetic chitosan with graphene oxide and to specify the optimal conditions for the adsorption.

2. Experimental
2.1 Materials and methods
The solvents and chemicals like chitosan, Fe3O4, potassium permanganate and graphite were purchased from Aldrich, USA with very high purity. Most of dilution was done using double distilled water.

2.2 Preparation of Graphene Oxide (GO)
In 500 ml beaker, 2 g of the purchased graphite powder and 1 g of (NaNO3) with 46 ml of (H2SO4) were mixed under magnetic stirring for 20 minutes at 25°C. 6 g of (KMnO4) were added to the mixture at 20 °C. After 5 minutes of stirring, the mixture was heated to 35 °C for 30 min, then 92 ml of distilled water was added to the mixture while stirring. After that, 80 ml of hot water (60 °C) was added to the mixture with (H2O2) (3% wt./wt.) to remove any remaining traces of (KMnO4) until the absence of bubbles in the solution. In the next step, centrifugation of the mixture at 6500 rpm for 45 minutes was occurred as described in ref. [27].

To neutralize the pH of the material that was obtained after centrifugation, sodium hydroxide (NaOH) was added again. Finally, the resultant product was obtained and the final product which is graphene oxide that is dark brown powder.

2.3 Preparation of Cross-linked magnetic chitosan with graphene oxide beads (CM/GO Bs)
A 0.1 gram of chitosan was dissolved in 15 ml (CH3COOH) in 250 ml beaker and the mixture was stored overnight. After that, 1.5 g of (Fe3O4) was added to the previous mixture. The above mixture was agitated for 2 hours at 60 °C.

In 5 ml ethanol, 0.05 ml of tetraethylorthosilicate (TEOS) was dissolved and then added dropwise to the above mixture.

Separately, 0.1 g of graphene oxide was dispersed in 200 ml distilled water, then the mixture was placed in ultrasonic bath in a 400-ml beaker for 1 hour.
Now, both magnetic chitosan solution and graphene oxide dispersion were mixed together at 60 °C. The mixture was stirred for 4 hours until the mixture became thick viscous liquid, then, the prepared mixture was placed on plastic plate and dried. The industrial sheets that were produced have a thickness of about 0.16 nm. Fig. 1 show all steps of the preparation.

Figure 1: Preparation of CM/GO Bs procedure

2.4. Sample characterization
The morphologies of the surface of cross-linked (CM/GO) were characterized using a cold field transmission electron microscope (TEM) (Inspect F50, Netherlands). To study the magnetic properties for the mixture, a vibrating sample magnetometer (Model 155, USA) was used. The range of magnetization was between 0 and 1 tesla at around 25 °C. to study the spectra of the prepared compound a Fourier Transform (FT-IR) Nicolet model 6700 was used. The operating conditions were: a range from 220 -3800 cm⁻¹, resolution of 4 cm⁻¹ was used with 128 scans.

2.5 Batch Adsorption Studies

2.5.1 Effect of pH and Co-existing Anions
The pH effect on adsorption was detected by making pH varied from 2 to 12 using HCl and NaOH solutions. In 50 ml perchlorate solution (15 ppm), 1.0 g CM/GO Bs is added. After that, the mixture was agitated at 200 rpm for 4 hours.
In order to determine zero-point charge, several masses CM/GO in the range 5–100 g/L using a 0.03 M KNO₃ solution. The aqueous suspensions were shaked for 24 h in a shaker at 300 rpm to reach a pH equilibrium. To obtain pHpzc a plot of equilibrium pH versus sorbent mass was done.

The effects of Cl⁻, NO₃⁻, SO₄²⁻ and HCO₃⁻ anions, on perchlorate adsorption were determined. The experiments of the study of the effect of co-existing anions were done using the same procedure of studying the effect of pH but in this case the pH was varied.

2.5.2 Effect of Contact Time

To study the kinetics of perchlorate adsorption, many various concentrations (5, 10, 15 and 20 ppm) were taken with constant 1 g/L adsorbent dosage and by shaking at 200 rpm at room temperature.

2.5.3 Effect of temperature

Aliquots of 1 g of each dry CM/GO Bzs were transferred into flasks each contained 50 ml perchlorate solution. The concentration of perchlorate ranging from 1 to 200 ppm. Each flask was agitated on a shaker at 180 rpm for 4 hours at (303, 313, and 323) K.

After that and when the equilibrium of the adsorption was reached, the solution was filtered and the concentration of perchlorate that remained in the solution was determined. All experiments was repeated 3 times.

The amount perchlorate that was adsorbed (qe, mg/g) was calculated by the equation [17]:

\[ q_e = \frac{V(C_o - C_e)}{W} \]  

(1)

Where V is the volume of the solution (L), C₀ is initial perchlorate concentration (ppm), Cₑ is perchlorate concentration at equilibrium (ppm), and W is the adsorbent mass (g).

2.6 Regeneration process

0.1 gram of CM/GO Bzs was added to 50 ml of 10 mg/L perchlorate solution and shake for 4 hours at 200 rpm. After that and when the equilibrium was reached, the adsorbent was collected by filtration.

The adsorbent was transferred into a flask contained 8 ml of 0.1 % solution of NaCl and stirred at 298 K for one hour. The adsorbent was filtered and collected.

To check the ability of regeneration of the adsorbents, many cycles of re-adsorption/desorption were tested.
2.7 Analytical Methods

To determine the perchlorate concentration, ion chromatography (compact IC, Metrohm) was used. The instrument of IC system consists of a 250 µL sample loop, a group of 4x250 mm chromatogram (Metroep A sup 7), a 4 mm suppressor, guard columns, an auto-sampler and electrical conductivity detector.

To detect perchlorate, the eluent that was used is a mixture of about 10 Mm (Na$_2$CO$_3$) and 45% acetonitrile (v/v) at a flow rate of 0.8 ml/minute. A time of 22 minutes was used to do the sample. The perchlorate detection limit was approximately 15 µg/L.

3. Results and Discussion

3.1 Material Characterization

3.1.1 FTIR Analysis

During modification and process of adsorption, there are many changes in functional groups, so, to show the changes in these functional groups, FTIR spectra was used. The study was taken by using CM/GO Bs loaded with ClO$_4^-$ . The FTIR spectrum for CM/GO Bs is shown in Fig.2 (a) A strong band from 1200 to 1400 cm$^{-1}$ was shown which means the stretching vibrations of epoxide functional groups. The band at 1625 cm$^{-1}$ represent the stretching of C=C, on the other hand, a peak at 1710 cm$^{-1}$ is showing carbonyl groups Fig.2 (b).

![Figure 2](image-url) (a) FTIR characterization of CM/GO Bs. (b) FTIR spectra of graphene chitosan.

3.1.2 TEM Analysis
Fig. 3 shows the TEM micrographs of the complex. It can be seen that CM/GO Bs has a square shape and porous internal structure. On the other hand, the shape of the surface is irregular which helps to improve the capability of its adsorption. Using optical microscopy, this will help in measuring both size and distribution. The particle size was 40-160 nm due to the existing of nano Fe$_3$O$_4$ as a framework. In previous study, a diameter of chitosan was found to be around 1.5 mm. [24], compared with our complex CM/GO which gives a larger spectra and lower size surface area that help in the activity of the reaction.

Figure 3: TEM analysis of CM/GO Bs complex.

3.1.3 VSM Analysis

To measure the magnetic property for the adsorbent a VSM was used. Fig. 4(a) shows the hysteresis loops of CM/GO Bs and naked Fe$_3$O$_4$ at 298 K. The magnetization of CM/GO was about 21.7 emu/g, while naked Fe$_3$O$_4$ was about 91.2. The lower in the magnitude of the magnetization between naked Fe$_3$O$_4$ and CM/GO polymer is due to interaction of chitosan and graphene. The response to an external magnetic field of the complex was rapid. On the other hand, and through the Fig. 4(b), CM/GO Bs complex may be collected quickly to the glass wall of the bottle using a piece of regular magnetic. Thus, good magnetize properties of CM/GO Bs complex may shows the magnetize process [25, 10].
3.1.4. Thermal Analysis

Thermal study (TGA) was used to investigate the stability and the formation of new compounds. This study was expressed using the weight loss derivative curve (DTG. Fig.5 shows two major steps of degradation for graphene chitosan. The first one ranges from 25 to 290 °C with mass loss of 9%. While the second one between 300 – 700 °C which show a decrease of 70% in mass and it appears almost at 460°C.

Figure 5: TGA and DTG curves of graphene chitosan.

3.1.5 XRD Characterization
For the graphene chitosan sample, the characteristic diffraction peak at 11.37° was appeared due to the amorphous character of chitosan. In the (CM/GO) sample, the peaks observed at 30.2° (220), 35.6° (311), 43.2° (400), 57.1° (511) and 62.7° (440) show the cubic inverse structure of Fe$_3$O$_4$. As shown in Fig.6.

![XRD spectrum of graphene chitosan, magnetic graphene chitosan.](image)

**Figure 6:** XRD spectrum of graphene chitosan, magnetic graphene chitosan.

### 3.2 The Effect of pH on Perchlorate Adsorption.

The effect of pH was carried in the range 2 to 12. The obtained results are presented in Fig. 7. Maximum adsorption of perchlorate by CM/GO Bs was obtained in the pH range 2-6.

![Experimental mass titration curves corresponding to CM/GO Bs.](image)

**Figure 7:** (a) Experimental mass titration curves corresponding to CM/GO Bs .(b) Effects of pH on the adsorption of perchlorate by CM/GO Bs complex.

In order to determine zero point charge, mass titration technique (MT) was used. When looking at Fig. 7 (a) and (b), it can be seen that zero-point charge equal 6.3 with a
maximum sorption values occurred at pH < pH\text{pzc}. Therefore, electrostatic attractions between positively charged surface of CM/GO Bs and ClO$_4^-$ ions could take place and contribute to sorption.

Due to the competition that is excessive chloride ions within the pH adjustment, when the pH dropped to 2.0, the capacity of adsorption of the adsorbent declined to 7.02 mg/g. The capacity of the adsorption declined strongly from 7.8 mg/g to 1.6 mg/g while the pH increases from 10.0 to 11.5. That is because of alkaline condition that causes a negative change of the surface of the adsorbent. Besides, it creates weak interaction between perchlorate and adsorbent in comparison with protonated cross-linked chitosan that has a range of pH from 4.0 to 10 that can be applied. CM/GO Bs may adsorb over- widened range of pH from (2-6), this property makes it useful for its adsorption process.

3.3 Effect of Co-existing Anions.

Polluted water usually contains many anions such as ClO$_4^-$, NO$_3^-$, Cl$^-$, SO$_4^{2-}$ and HCO$_3^-$. The presence of other anions along with perchlorate made the other ions to compete with perchlorate on adsorption on the adsorbent, which caused a decreasing in the capacity adsorption of perchlorate [26].

As shown in Fig.8 that studied the consequences of these anions and plotted, this increase in concentration leads to a decline in the adsorption of perchlorate. The presence of other anions along with perchlorate made the other ions to compete with perchlorate on adsorption on the adsorbent, which caused a decreasing in the capacity adsorption of perchlorate [27]. In addition, SO$_4^{2-}$ anion has the greatest impact on perchlorate that removed. As an increasing in the concentration of SO$_4^{2-}$ from 0 to 28 mg/L, the capacity of perchlorate adsorption by CM/GO Bs complex sharply declined from 7.5 mg/g to 3.3 mg/g. Finally, the inhibitory effects of these anions on perchlorate adsorption by CM/GO was summarized as: SO$_4^{2-} <$ NO$_3^- <$ Cl$^-$, which agrees with last studies. This would be explained due to the larger charge of $-2$ on the sulfate anion (SO$_4^{2-}$) than $-1$ for chloride [27,28].
3.4. Effect of Contact Time

Effect of contact time is very important in treatment of wastewater. To obtain the most suitable contact time of the reaction, many different initial concentration (5, 10, 15 and 20 mg/L) are studied with adjusting other conditions such as dosage of the adsorbent which was 1 g/L, pH which was 6 and temperature that was 303 K. Fig. 9 shows the effect of contact time on the capacity of perchlorate adsorption.

The adsorption of perchlorate was quick at the first 25 minutes, then the adsorption rate declined, and the equilibrium was achieved within 35 minutes. When the initial concentration of the perchlorate was small, the adsorption reached equilibrium within 25 minutes. The residual content of the perchlorate was 0.014 mg/L which agrees with the Drinking Water Health Advisory Board with level of 15 mg/L that was studied by the United States Environmental Protection Agency in 2008[29].
It can be concluded that the rate of the adsorption of perchlorate by the complex is quick and removing of perchlorate by the complex was efficient at low concentrations.

3.5 Adsorption Kinetics

To obtain the mechanism of the reaction and the rate determining step, results that shown in Fig.9 must be analyzed, that’s occurred by studying three models of kinetics. We used the pseudo-first-and-second-order models, and described the equations of these models as [29]:

\[
\frac{1}{q_t} = \frac{k_1}{(q_e t)} + \frac{1}{q_e} \quad (2)
\]

\[
\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{1}{q_e} t \quad (3)
\]

while \( k_1 \) means the constant of the adsorption rate of the pseudo-first- order (h\(^{-1}\)); \( k_2 \) stands for the constant of the adsorption rate of the pseudo-second-order ((g/mg)h); \( q_e \) represents the amount of ions adsorption at equilibrium (mg/g) and \( q_t \) shows the amount of ion adsorption amount (mg/g). By the slope of the linear equation, the values of \( k_1 \) and \( k_2 \) can be estimated using equations from plots. In Table1, the rate constants and correlation coefficient (\( R^2 \)) of the models of kinetic are lodged.
Fig. 10: The Pseudo-first-order plots for perchlorate adsorption onto CM/GO Bs

Fig. 11: The Pseudo-second-order plots for perchlorate adsorption onto CM/GO Bs

Table 1: correlation coefficients and constants of kinetic model of perchlorate adsorption onto CM/GO Bs.

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qe (exp)</td>
<td>1.2</td>
<td>4</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td><strong>Pseudo first order</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_1$ (min$^{-1}$)</td>
<td>0.991</td>
<td>12.919</td>
<td>0.448</td>
<td>0.39</td>
</tr>
<tr>
<td>$q_e$ (mg/g)</td>
<td>1.104</td>
<td>2.98</td>
<td>5.69</td>
<td>8.3</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.341</td>
<td>0.2302</td>
<td>0.309</td>
<td>0.348</td>
</tr>
<tr>
<td><strong>Pseudo second order</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Using the data listed in the Table 1, the correlation coefficient of the pseudo-second-order models were approx. 0.999 at the latter concentrations. This proves that the pseudo-second-order model reflects the experiment data accurately. While the correlation coefficient of the pseudo-first order models gave low values between 0.2 and 0.3 which is not appropriate to interact the adsorption mechanism.

Also, from Table 1, to find the kinetic model which fits our study both the calculated values of the amount adsorbed at equilibrium (q_e, calc) and the experimental (q_exp) were determined. The (q_e, calc) and the experimental (q_exp) were very close in the pseudo-second order model which proves that the adsorption follow this model.

Because the pseudo-second-order model is suitable for the mechanism, then the rate determining step may be chemisorption including electron participating or replacing between adsorbent and adsorbate [30] so, chemisorption may be the rate-determining step in the adsorption mechanism, and the obtained resulted from mass transfer in solution was restricted [31].

To examine the diffusion mechanism, the intra-particle diffusion model was presented. The equation of the model is given as [32]

\[ q_t = k_{pi} t^{1/2} + c_i \]  

Where \( k_{pi} \) (i=1-3) means the constant of the rate of the intra-particle diffusion (mg/g h^{1/2}) and (i) stands for the number of the levels of the particle such as \( k_{p1} \) is the constant in the first level of the external surface adsorption and \( k_{p3} \) is the constant of the rate in the third final equilibrium layer. The constants of the rate are shown in Table 1.

Within 25 minutes, the adsorption of the external layer was completed. During increasing in initial concentration, the \( k_{p1} \) shows a significant increased due to the increasing in the concentration of gradient force [33]. The rate determining step of adsorption isn’t intra-particle diffusion [34-35] because the linearity of the second and the third layers couldn’t pass through the origin.

<table>
<thead>
<tr>
<th>K_2 (min^{-1})</th>
<th>q_e (mg/g)</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.176</td>
<td>1.198</td>
<td>0.9948</td>
</tr>
<tr>
<td>0.105</td>
<td>4.11</td>
<td>0.9967</td>
</tr>
<tr>
<td>0.036</td>
<td>8.3</td>
<td>0.9985</td>
</tr>
<tr>
<td>0.0035</td>
<td>19</td>
<td>.9227</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>K_id</th>
<th>C</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.35</td>
<td>-</td>
<td>0.789</td>
</tr>
<tr>
<td>18.60</td>
<td>0.496</td>
<td>0.0882</td>
</tr>
<tr>
<td>37.96</td>
<td>1.17</td>
<td>0.882</td>
</tr>
<tr>
<td>45.81</td>
<td>1.082</td>
<td>0.932</td>
</tr>
</tbody>
</table>
Moreover, $k_{p,2}$ and $k_{p,3}$ are less than $k_{p,1}$ which means that the rate determining step is the external surface adsorption.

### 3.6 Adsorption Isotherm

The adsorption affinity and surface properties can be expressed by adsorption equilibrium isotherm through certain constants [36]. These isotherms were studied at 303, 313 and 323 k using a 10 ppm of perchlorate. To describe the adsorption process, we used Langmuir, Freundlich and Temkin models. The linear relations of these models are given as [36-37]:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$  \hspace{1cm} (5)

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (6)

$$q_e = B \log K_T + B \log C_e$$  \hspace{1cm} (7)

Where $C_e$ represents the concentration of perchlorate at equilibrium (ppm), $q_e$ means the amount of perchlorate that adsorbed at equilibrium (mg/g), $Q_0$ stands for the amount of adsorbed at complete coverage (mg/g), $b$ is Langmuir constant reflecting the energy adsorption in (L/mg). $K_f$ represents the constant of Freundlich that relates to the capacity of adsorption and $1/n$ means the intensity of the adsorption.

$K_T$ is the Tempkin constant that represent the maximum energy of bindings and $B$ is the Tempkin constant that represents the changing in the heat of the adsorption.

![Freundlich isotherm plot for perchlorate adsorption onto CM/GO Bs](image)

**Figure 12:** Freundlich isotherm plot for perchlorate adsorption onto CM/GO Bs
Figures 12, 13, and 14 show the equilibrium data for perchlorate adsorption in Freundlich, Langmuir, and Tempkin models. From the linear equations of the models, their constants may be determined from the slopes and intercepts. In Table 2, the correlation coefficient ($R^2$) and theoretical parameters of the models of adsorption isotherm are given.
Table 2: parameters and correlation coefficients of the adsorption isotherm models of perchlorate adsorption onto CM/GO Bs.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Q₀ (mg/g)</th>
<th>b (L/mg)</th>
<th>R²</th>
<th>R_L</th>
<th>K_F</th>
<th>1/n</th>
<th>R²</th>
<th>K_T</th>
<th>B (L/g)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>28.153</td>
<td>0.068</td>
<td>0.973</td>
<td>0.595</td>
<td>0.215</td>
<td>0.654</td>
<td>0.991</td>
<td>18.707</td>
<td>2.654</td>
<td>0.791</td>
</tr>
<tr>
<td>313</td>
<td>28.352</td>
<td>0.062</td>
<td>0.957</td>
<td>0.617</td>
<td>0.232</td>
<td>0.633</td>
<td>0.985</td>
<td>11.766</td>
<td>2.828</td>
<td>0.788</td>
</tr>
<tr>
<td>323</td>
<td>26.455</td>
<td>0.061</td>
<td>0.960</td>
<td>0.621</td>
<td>0.290</td>
<td>0.595</td>
<td>0.962</td>
<td>5.922</td>
<td>3.013</td>
<td>0.844</td>
</tr>
</tbody>
</table>

Through the correlation coefficients ($R^2$) especially in Langmuir and Freundlich isotherms that have values of ($R^2$) more than 0.90, while if we look to the value of $R^2$ in Tempkin that is less than 0.85. In general, and in a previous studies, if Langmuir model data fitted the experiment well this means that the surface is homogenous one and consists of one layer (mono layer) and the process of adsorption is physisorption, on the other hand, if the Freundlich model data fitted well, this means that the surface is heterogeneous and the process will be chemisorption[38].

Through the above results, the process of the adsorption was a complex of homogenous and heterogeneous, whereas the effect of adsorbent interactions on the adsorption was finite. So, both physisorption and chemisorption are important in the process of adsorption.

If we made a comparison between heavy metal adsorption by magnetic adsorbent and perchlorate adsorption by our complex (CM/GO Bs), big difference will be noted in which of most of the adsorption agreed with chemistry and the main mechanism of perchlorate removal and most of them show Langmuir model [39]. In the Freundlich isotherm model, 1/n values were ranged from 0.1 to 1 at different temperatures, that proves the mechanism of the adsorption was favorable by the model of Langmuir isotherm. The temperature in the adsorption process was insignificant due to the slightly changing in the optimum adsorption capacity with increasing in temperature.

Dimensionless constant term that is the essential property of the Langmuir isotherm can be determined through eq. 4.7. The equilibrium parameter $R_1$, which is determined as follows [40]:

$$R_L = 1/(1 + bC_0)$$  \hspace{1cm} (8)

Where $C_0$ represents the initial concentration of perchlorate (ppm) and $b$ means the constant of Langmuir isotherm (L/mg). The $R_L$ values indicate the irreversibility, linearity and favorability of the adsorption such as if ($R_L=0$) this means that the
adsorption is irreversible, if \((R_L\) larger than 0 and less than 1), this means that the adsorption is favorable or if \((R_L=1)\) this means that adsorption is linear or unfavorable \((R_L>1)\). All values of \(R_L\) that given in Table 2 above lead to an impact that the adsorption of perchlorate on CM/GO Bs was favorable at all temperatures that were studied. Through the results, as the initial concentration of perchlorate increase, the \(R_L\) values decrease due to the increasing in concentration of driving force ingredient with increase in initial concentration [9].

3.7 Adsorption Thermodynamics

One of the aims in this work is to determine the parameters of thermodynamics of the adsorption of the perchlorate on CM/GO Bs. The experiments of the adsorption were carried out at 303, 313, 323k. The initial concentration of perchlorate was adjusted at 15mg/L. In order to determine the free energy of the adsorption \((\Delta G)\), the equation of the Gibbs free energy is used [30]:

\[
\Delta G = -RT\ln k_c
\]

(9)

Where \(R\) represents the gas constant \((8.314 \text{ J/mol k})\), \(T\) stands for temperature of the adsorption in Kelvin, and \(k_c\) means the constant of the adsorption at equilibrium in \((\text{L/g})\). According to the equation (4.9), The \(k_c\) values of equilibrium at any temperature can be calculated as follows:

\[
K_c = \frac{q_e}{C_e}
\]

(10)

Where \(q_e\) represents the amount of adsorption at equilibrium in \((\text{mg/g})\) and \(C_e\) stands for the concentration of perchlorate at equilibrium in \((\text{mg/L})\).

By plotting in \(\ln k_c\) vs \(1/T\) according to the following equation:

\[
\ln k_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}
\]

(11)

The entropy of adsorption \((\Delta S^o)\) and standard enthalpy \((\Delta H^o)\) can be determined.

The negative value of the slope multiplied \(R\) represents \((\Delta H^o)\), and the intercept multiplied \(R\) represents \((\Delta S^o)\) of the adsorption of perchlorate (Fig.15).
Figure 15: The thermodynamic study for perchlorate adsorption onto CM/GO Bs

The three thermodynamics parameters ($\Delta G^o$, $\Delta S^o$ and $\Delta H^o$) are listed in Table 3. Through the results in Table.3, the entropy is negative. This means that the random state at the solid/solution interface decreasing. Through the data that are given in table 3, the negative values of Gibbs standard free energy at many various temperatures leads the adsorption of perchlorate onto CM/GO Bs process spontaneous. So, the effect of temperature on the process of adsorption was insignificant, because there is no energy input required from the outside of the system of the change in standard free energy that was not affected with increasing temperature. In addition, and due to the negative values of enthalpy, the process of the adsorption was exothermic one. The values of enthalpy were less than 40 kJ/mol. This indicates that the adsorption is physisorption [41 -42]. In addition, theoretically, the changes in energy for physisorption are ranged from 0 to -20 kg/mol, while those for chemisorption are ranged from 80 to 400 kJ/mol.

Table 3: parameters of thermodynamic for adsorption of perchlorate onto CM/GO Bs

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$K_c$</th>
<th>$\Delta G^o$ (KJ/mol)</th>
<th>$\Delta H^o$ (KJ/mol)</th>
<th>$\Delta S^o$ J/mol K</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>2.852</td>
<td>-2.673</td>
<td>-9.773</td>
<td>-22.811</td>
</tr>
<tr>
<td>323</td>
<td>2.264</td>
<td>-2.231</td>
<td>-9.773</td>
<td>-22.811</td>
</tr>
</tbody>
</table>

The free energy of adsorption ranged from -2.231 to -2.673 kJ/mol for CM/GO Bs. This suggests that the adsorption likely resulted because of physical sorption. In general, there are different types of interaction according to how pollutants interact with composites of
magnetic chitosan including ion exchange, chemical bonding, hydrogen bonding and physisorption [11]. The most important driving force in this study was electrostatic interaction between anion that was perchlorate and cations which were (amine groups) of the adsorbent.

In resultant, according to data that determined in this study of the adsorption kinetics tells us that the adsorption was pseudo-second-order that suggests a chemisorption, while according to adsorption thermodynamics and isotherms, the process was physisorption, such that anions bind to the CM/GO Bs surface by intermolecular interactions [42-44]. In resultant, the adsorption of perchlorate on CM/GO Bs is a complex physical and chemical adsorption process.

3.8 Regeneration ability

Regeneration of the complex is very important to decrease the costs, to be used for several times and to be recycled of useful material. The used adsorbent was eluted using 0.1% sodium chloride.

To check the ability of regeneration of the adsorbents, many cycles of re-adsorption/desorption were tested. In this study, five cycles were tested with adjusted conditions, and the results are shown in Fig.16.

The capability of the adsorption of the regeneration adsorbent decreased a few amounts after five cycles. On the other hand, the capacity of the adsorption changed from 7.8 to 6.2 mg/g due to loss of adsorbent and decrease of the reaction sites on adsorbents.
Figure 16: Capacity of perchlorate adsorption onto CM/GO Bs with five re-adsorption/desorption cycles

Conclusion

In our study, CM/GO Bs was produced and applied for perchlorate removal from wastewater. The magnetic power of the CM/GO Bs complex showed about 21.8 emu/g, which was sufficient for its high recovery using an external magnetic field. The CM/GO Bs complex could adsorb perchlorate efficiently at a wider range of pH than raw chitosan which was from 4 to 10.

Co-existing anions, especially SO$_4^{2-}$, will affect the perchlorate adsorption onto CM/GO Bs.

The rate of adsorption was very fast and reached equilibrium within 35 minutes. The adsorption data followed the pseudo-second-order model. Langmuir and Freundlich isotherms were studied and followed Langmuir isotherm. The enthalpy and Gibbs standard free energy showed that the adsorption phenomena was exothermic and spontaneous. Perchlorate adsorption on CM/GO Bs was a very complex chemical and physical adsorption process. The fluctuated adsorbent could be regenerated in an efficient and economic using NaCl eluent. CM/GO Bs complex exhibits a good efficiency for removal of perchlorate as an environmentally friendly adsorbent, over a wide pH range and with good regeneration and recovery ability.

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