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Adsorptive removal of permanganate anions from synthetic wastewater using copper sulfide nanoparticles

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Abstract

The performance of Copper Sulfide (CuS) was evaluated as sorbent material for Permanganate ions (MnO$_4^-$). The influences of pH, MnO$_4^-$ concentration, sorption time and temperature were inspected. The outcomes of this study approved that the sorbate primary concentration of 1200 mg L$^{-1}$, solution pH of 1.5, 90 min sorption time and temperature of 60 $^\circ$C are the optimal conditions for MnO$_4^-$ sorption by CuS. The study also revealed that the kinetic model of second order and model of Langmuir isotherm describe well the experimental data of this sorption. Furthermore, significant sorption capacities of 769.23, 909.09, 1111.11 and 1250.00 mg g$^{-1}$ were resulted at 20 $^\circ$C, 30 $^\circ$C, 40 $^\circ$C and 60 $^\circ$C, one-to-one. Additionally, thermodynamic outcomes confirmed that the nature of MnO$_4^-$ sorption by CuS is a heat-absorbing and spontaneous.

1. Introduction

One of the most common chemical reagents used in this century is KMnO$_4$, which is mainly included as an oxidant in many medical and industrial activities [1]. The odors, plant’s growth, taste and the processes of disinfectants production are usually controlled by this oxidant [2]. Currently, it is increasingly used as a powerful and effective oxidant to get rid of chlorinated solvents that contaminate soil and ground water [3]. It is also used to rapidly treat of the chlorinated ethane compounds [3]. Besides, KMnO$_4$ was used for extraction of dyes, cyanide, manganese, iron and phenols from some factory’s wastewaters [4, 5]. Nevertheless, it is inopportune that the waters will be contaminated by MnO$_4^-$ anions due to its negative effects on human skin and eyes [6]. Furthermore, consuming solutions with a high concentration of this compound can be potentially deadly [6].

Therefore, the technique of Fluidized-Bed Crystallization was applied by Li et al. [7] to remove wastewater produced by factories from MnO$_4^-$ anions. Adsorption is considered as an effective and excellent method to remove MnO$_4^-$ anions from solution. In this technique, activated carbon of coconut shells [8], bone and corncob [9], and others have been used for MnO$_4^-$ anions sorption from solution. Despite the significant performance of activated carbon for MnO$_4^-$ anions sorption, its production needs higher energy and potentials. Therefore, the modified powders of Nitraria retusa [10], Neem [11] and sage leaves [12] were used as cheap sorbent for MnO$_4^-$ anions elimination from its solutions.

Owing to the significant adsorptive advantages of the nano-particles of metallic oxides (great adsorption capacity and higher sorption rate), sorption of various pollutants by these metallic oxides was investigated [13–19].

CuS is one of the metallic sulfide’s nanoparticles used in semiconductors and electrochemical sensors [20]. The nanoparticles of CuS were composited with graphene and used for the sorption of methylene blue [21], the synthesized CuO-CuS nano porous was applied for sorption of negatively charged contaminants from waste water [22], and activated carbon was also loaded by CuS and used for the elimination of ternary dye from solutions [23].

Although all of these studies confirmed that CuS displayed very good adsorption efficiencies towards various pollutants, no effort has been achieved to examine the adsorption efficiency of CuS towards MnO$_4^-$ anions.
Therefore, this study aimed to investigate the ability of this sorbent for the sorption of MnO$_4^-$ anions. The sorptive properties of CuS, impacts of experimental conditions and adsorption constants will be examined in this research.

2. Chemicals and methodology

2.1. Chemicals
Copper sulfide (CuS, M.W: 95.61 g mol$^{-1}$, mp: 220 °C and d: 4.6 g ml$^{-1}$ at 25 °C), potassium permanganate (KMnO$_4$), Sodium Hydroxide (NaOH), Sodium Carbonate (Na$_2$CO$_3$) and Hydrochloric Acid (HCl) were supplied by Merck (Dermasdat, Germany) and used in this work without any additional purification.

2.2. Methodology

2.2.1. Characterization of CuS
CuS was scanned by SEM before and after sorption of MnO$_4^-$ to identify the surface morphology of this sorbent. The surface analyzer of BET (NOVA-2200 Ver. 6.11) was also performed at the suitable conditions to determine the surface area and porosity of CuS. Moreover, a 0.5 l of 0.001 M Na$_2$CO$_3$ was prepared, 30 ml of this solution was added to each one of six plastic beakers (100 ml), and then drops of 0.2 M of NaOH or HCl were added to each one of these solutions to prepare six solutions with various pH values (1, 3, 5, 7, 9, 11), after that, each one of these solutions was mixed with 0.2 g of CuS in 50 ml plastic bottle. These plastic bottles were agitated by shaker incubators at 30 °C and 180 rpm for 20 h, pH meter was used for measuring the final pH of each solution after filtration (pHf). The same procedures were repeated for another two solutions of Na$_2$CO$_3$ with concentrations of 0.05 and 0.1 M. The difference between the values of the initial pH (pHi) and final pH (pHf) was computed for each solution. Finally, the relationship between (pHf–pHi) and pHf was graphed to estimate the value of pHZPC for CuS.

2.2.2. Adsorption experiments

2.2.2.1. Impact of CuS dosage
20 ml of 600 mg l$^{-1}$ of MnO$_4^-$ anions solution was mixed with 0.005 g of CuS in an amber bottle. This mixture was agitated in shaker incubators at the original pH solution of KMnO$_4$, 30 °C and 180 rpm for 20 h. The spectrophotometer of 6800UV-visible (Jenway, UK) was used for measuring the final concentration of KMnO$_4$ at the $\lambda_{max}$ of 525 nm. Similar processes were repeated but with various amounts of CuS (0.01, 0.015, 0.02, 0.025, 0.03, 0.035, 0.04 g). The percentage removal was calculated for each amount by using equation (1).

$$\%R = \left(\frac{C_0 - C_e}{C_0}\right) \times 100$$

Where, $C_0$ and $C_e$ are the KMnO$_4$ concentration at zero time and equilibrium time.

Finally, the values of the percentage removal were plotted via the mass of the sorbent to demonstrate the effect of the sorbent dose on this sorption.

2.2.2.2. pact of pH
0.2 M of HCl and/or NaOH solutions were used for preparation MnO$_4^-$ anions solutions with various pH values (1.5–11) and initial concentration of 500 mg l$^{-1}$. A 20 ml of each solution was added with 20 mg of CuS to amber bottle (30 ml) and shaken for 20 h in shaker incubators at 165 rpm and 30 °C. After the separation of CuS from the mixtures by filtration, the remaining concentration of MnO$_4^-$ of each solution in the filtrate was measured as mentioned in section 2.2.2.1. And then, the equilibrium sorption quantities ($q_e$) were computed from the equation (2) and plotted against pH to illustrate the influence of pH on this sorption.

$$q_e = \frac{V}{m}(C_0 - C_e).$$

Where, $q_e$ (mg g$^{-1}$): concentration of KMnO$_4$ before adsorption, $C_e$: concentration of MnO$_4^-$ (mg l$^{-1}$) after equilibrium, m: adsorbent mass (g), V: volume of adsorbate solution (l).

2.2.2.3. Batch Kinetic experiments
A fixed mass of CuS (0.02 g) was added to three bottles of amber each containing 20 ml of MnO$_4^-$ solutions with different concentrations (400, 500, and 600 mg l$^{-1}$). Those bottles were agitated by shaker incubator for 5 min at 30 °C, 165 rpm and original pH solution. Then the three mixtures were filtered and the sorbate (KMnO$_4$) residual concentration in each one of the three suspensions was measured by the UV–vis spectrophotometer at $\lambda_{max}$ of 525 nm. The same experiment was also carried out with different contact times (15, 30, 45, 90, 180, 300,
and 420 min) to study the influence of agitation time and to identify the equilibrium time of this sorption. Equation (3) was used for computing the sorption amount of each time ($q_t$).

$$q_t = \frac{V}{m}(C_0 - C_t).$$  \hspace{1cm} (3)

$V$: MnO$_4^-$ anions solution volume (L), $m$: CuS mass (g), $C_0$ and $C_t$ are the MnO$_4^-$ anions concentrations at sorption contact time zero and $t$, respectively.

The data shown in this section was also analyzed by $t$ models of kinetic that are listed in table 1 to determine the rate and kinetic constants of this sorption.

2.2.2.4. Batch equilibrium experiments

The MnO$_4^-$ anions experimental solutions with the required concentrations (400, 500, 600, 700, 800, 1000, 1200, 1300, 1400, 1500 mg L$^{-1}$) were prepared. 20 ml of each solution was put with 0.02 g of CuS in bottle of amber (30 ml). After tight capping, the bottles were shaken by a thermal shaker for 20 h at 165 rpm, original pH and 20°C. The MnO$_4^-$ anions solutions were then disconnected from CuS by filtration and the remaining concentration of MnO$_4^-$ anions in each suspension was measured as mentioned in section 2.2.2.3. This experiment was repeated at temperatures of 30°C, 40°C and 60°C. Equation (4) was applied for calculating the sorption quantities at equilibrium ($q_e$ mg g$^{-1}$).

$$q_e = \frac{V}{m}(C_0 - C_e).$$  \hspace{1cm} (4)

$C_0$ and $C_e$: MnO$_4^-$ anions concentrations before sorption and at equilibrium, respectively, $m$: CuS mass, $V$: MnO$_4^-$ anions solution volume (L).

The obtained values of $q_e$, at each temperature were plotted against $C_0$ to explore the impacts of temperature and initial concentration of MnO$_4^-$ anions solution on this sorption. The models of isotherms listed in table 2 and equation (5) were also applied for analyzing the experimental data of this part.

$$R_L = \frac{1}{1 + K_L C_0}. \hspace{1cm} (5)$$

$C_0$: highest MnO$_4^-$ anions initial concentration $K_L$: constant of Langmuir.
Moreover, the changes in standard free energy ($\Delta G^\circ$), entropy ($\Delta S^\circ$), and enthalpy ($\Delta H^\circ$) for sorption of 1300, 1400 and 1500 mg l$^{-1}$ MnO$_4^-$ anions on the surface of CuS were computed by applying equations (6) and (7).

$$\ln \left( \frac{q_e}{C_e} \right) = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$  (6)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$  (7)

$T$: adsorption temperature (K), and $R$: the universal constant of gases (8.314 J K$^{-1}$ mol$^{-1}$).

3. Results and Discussion

3.1. Characterization results

The structures of surface of CuS NPs before and after MnO$_4^-$ sorption are as depicted in figures 1 and 2, respectively. Bulky holes as well as unequal macropores can be observed on the surface of CuS before sorption of MnO$_4^-$ anions (figure 1). The presence of these big holes and irregular macropores will allow the MnO$_4^-$ anions to pass easily through the surface of CuS during the process of adsorption. It can also be noted from figure 2,
most of the bulky holes and unequal macropores have been disappeared from the surface of CuS due to sorption of \( \text{MnO}_4^- \) anions on the surface of this sorbent.

The plot of \( \text{pH}_i \) vis \( \text{pH}_f \) is shown in figure 3. This figure depicts that the surface of CuS will be positively charged, uncharged and negatively charged at \( \text{pH} < 7 \), \( \text{pH} = 7 \) and \( \text{pH} > 7 \), respectively.

The outcomes of the BET surface analyzer showed that CuS has a significant surface area \((798.91 \text{ m}^2\text{g}^{-1})\), total pore volume of 0.00051 c.c./g and 40.585 Å average pore diameter.

### 3.2. Adsorption results

#### 3.2.1. Influence of CuS dose

The calculated percentage removal (% R) of \( \text{MnO}_4^- \) anions from aqueous phase was graphed against CuS dosage (figure 4) to investigate the effect of the sorbent amount on the sorption capacity and to determine the optimal dose of CuS that can be used in this work. As shown in figure 4, the value of % R is increased when the dosage of CuS increased from 0.005 g to 0.02 g. This augment due to the increment of the sorption active sites which are normally increased by increasing the sorbent dosage [23]. Then % R almost be constant when the dose elevated over 0.02 g which can be explained by the fact that the molecules of the sorbent at the higher dosages will be assembled or conglomerated together forming a cluster [24]. Therefore, 0.02 g of this sorbent was considered as the optimal amount and it was also used for performing the other experiments.

#### 3.2.2. Influence of pH

The most crucial factor that affects the sorption, is the pH of the adsorbate aqueous solution due to its effective influence on the sorbent surface charge and the ionization degree of the adsorbate [25]. Therefore, the effect of this parameter on the sorption of \( \text{MnO}_4^- \) by CuS was examined (figure 5). A slight decrease in the amount of \( \text{MnO}_4^- \) uptake by CuS occurred when the pH augmented from 1.5 to 7 (figure 5). This can be elucidated by the fact that the sorption in this range of pH (1.5–7) obtained due to the force of attraction between the positively charged surface of CuS \((\text{pH}_{ZPC} = 7)\) and anions of \( \text{MnO}_4^- \). The positive charges on the surface of CuS gradually and slightly decreased as the pH values rose from 1.5 to 7 causing slightly and gradually decreasing in the attraction force between \( \text{MnO}_4^- \) and the positive charges of the sorbent surface. Figure 4 also illustrates the sudden decrease of the sorption amount when the pH value surpassed 7 because of the repulsion force between \( \text{MnO}_4^- \) and the CuS surface which becomes negatively charged \((\text{pH} > \text{pH}_{ZPC})\). Figure 5 also shows that 1.5 is the pH optimal value in this sorption.
3.2.3. Kinetic studies

The calculated amounts adsorbed by CuS (\(q_t\)) for each one of the three solutions of KMnO₄ (400, 500 and 600 mg l⁻¹) were plotted against the sorption contact time (\(t\)) (figure 6) to identify the equilibrium time of this sorption and to explore the influence of agitation time. As shown in figure 6, the quantity of MnO₄⁻ anions adsorbed by CuS for each concentration is gradually augmented by increasing the time of sorption from 0 to 90 min and no changes in the values of \(q_t\) were obtained when the contact time increased above 90 min. This can be explained by the fact that all of sorption effective sites were empty at the beginning, then these sites gradually filled with anions of MnO₄⁻ during the sorption contact time ranged from 0 to 90 min, after that there is none of the sites were vacant to adsorb extra anions of MnO₄⁻. Similar outcomes were reported for MnO₄⁻ sorption by the leaves powder of Nitraria retusa and Neem [10, 11]. Although, 90 min is the equilibrium contact time of this sorption, the experiments related to the effect of CuS dosage, influence of contact time, isotherms and
thermodynamics were performed at 20 h for more confirmation that all of this sorption parameters were actually investigated at equilibrium.

Moreover, the experimental data of this part was analyzed by applying the kinetic models of 1st order (figure 7), 2nd order (figure 8) and intra-particle-diffusion (figure 9). The kinetic constants of this sorption were calculated from intercepts and slopes of the plots of these three figures. The values of these constants were registered in table 3 (1st, 2nd order models) and table 4 (intra-particle-diffusion). The results in table 3 indicate that all plots of 2nd order model are linear because the values of $R^2$ (coefficient of correlation) are almost equal to unity, whereas, the plots of 1st order model are non-linear ($R^2 < 0.900$). Furthermore, table 3 demonstrates that the values of $q_{e,exp}$ ($q_e$, experimental) are almost equal to values of $q_{e,cal}$ ($q_e$, calculated using 2nd order model) and there is a significant difference between values of $q_{e,exp}$ and $q_{e,1,cal}$ ($q_e$, calculated using 1st order model). These outcomes approve that the kinetic experimental data for MnO$_4^-$ sorption by CuS can be described by using the model of 2nd order better than 1st order. This designates that CuS adsorb MnO$_4^-$ anions by forming chemical bonds (chemisorption).

Figure 9 reveals the non-linearity of the three plots over the whole period of time and each plot consists of two linear sections with higher $R^2$ values. This designates that the MnO$_4^-$ anions adsorbed by CuS in several steps. Additionally, the C parameter which is related to the depth of boundary layer has high values, which confirms the importance of the external dispersion in this sorption [26]. The same outcomes were observed for MnO$_4^-$ sorption by the leaves powder of Neem [11].

### 3.2.4. Equilibrium outcomes

The amounts of MnO$_4^-$ adsorbed by CuS at equilibrium ($q_e$) and at four different temperatures were calculated by applying equation (4) for each one of the ten MnO$_4^-$ solutions. The calculated values of $q_e$ were plotted against the initial concentrations of MnO$_4^-$ ($C_0$) (figure 10) to examine the influences of the sorbate initial concentration and temperature on this sorption. As can be noted from figure 10, the values of $q_e$ are augmented by rising $C_0$, values from 400 to 1200 mg l$^{-1}$, because increasing the sorbate concentration will increase the dynamic force that has ability to diminish the resistance of MnO$_4^-$ anions mass movement at the sorbent and sorbate interface [27, 28]. It can also be noted from figure 10, that there are no variations in $q_e$ values when

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**Table 3.** The constants related to the 1st order, 2nd order kinetic models and experimental $q_e$ values for MnO$_4^-$ anions by CuS nanoparticles.

| $C_0$ (mg l$^{-1}$) | $q_{e,exp}$ (mg g$^{-1}$) | $q_{e,1,cal}$ (mg g$^{-1}$) | $K_1$ (h$^{-1}$) | $R^2$ | $q_{e,2,cal}$ (mg g$^{-1}$) | $K_2$ (g mgh$^{-1}$) | $R^2$ |
|---------------------|--------------------------|----------------------------|------------------|-------|--------------------------|---------------------|-------|
| 400                 | 397.14                   | 56.45                      | 0.0228           | 0.739 | 400.00                   | 0.000595            | 0.999 | 0.23810 |
| 500                 | 496.18                   | 89.58                      | 0.0223           | 0.716 | 500.00                   | 0.000360            | 0.999 | 0.18018 |
| 600                 | 595.12                   | 154.67                     | 0.0269           | 0.819 | 588.24                   | 0.000273            | 0.999 | 0.16191 |

**Table 4.** The constants related to the intra-particle diffusion kinetic model for MnO$_4^-$ anions by CuS nanoparticles.

| $C_0$ (mg l$^{-1}$) | $K_{dif}$ (mg/h$^{1/2}$/g) | $C$ | $R^2$ | $K_{dif}$ (mg/h$^{1/2}$/g) | $C$ | $R^2$ |
|---------------------|-----------------------------|-----|-------|-----------------------------|-----|-------|
| 400                 | 43.671                      | 103.69 | 0.991 | 0.0521                      | 396.06 | 0.951 |
| 500                 | 59.478                      | 83.98  | 0.991 | 0.0626                      | 494.80 | 0.865 |
| 600                 | 63.311                      | 122.39 | 0.993 | 0.0819                      | 593.48 | 0.986 |

**Figure 10.** Influence the temperature and initial concentration of MnO$_4^-$ solution on the sorption performance.
KMnO₄ concentration augmented over 1200 mg L⁻¹, because CuS has no vacant effective site to receive extra anions of MnO₄⁻ [27, 28]. Furthermore, figure 10 reveals the positive influence that temperature has on this sorption (endothermic process), because the viscosity of the liquid phase and the dynamic energy of MnO₄⁻ anions decreased and increased respectively due to the elevation of temperature [29]. Similar outcomes were reported for MnO₄⁻ sorption by the leaves powder of Nitraria [10].

Additionally, the equilibrium experimental data was analyzed by the linear isotherm models of Langmuir (figure 11), Freundlich (figure 12) and Temkin (figure 13). The values of isotherm parameters listed in table 5 were calculated from slopes and intercepts of the plots of these three figures. It can be noted that the plots of figure 11 (Langmuir model) are more linear than that of figure 12 (Freundlich model) and 13 (Temkin model). Moreover, R² (coefficient of correlation) values of Langmuir model are higher than that of Temkin and Freundlich models. These outcomes confirm that the equilibrium experimental data of this sorption are better described by the model of Langmuir than the other two models, which indicates the homogeneity of the sorption effective sites and monolayer sorption [18]. R_L (factor of dimensionless sorption) values and values of 1/n (table 5) are ranged from 0.0002 to 0.1052 and from 0.114 to 0.227, respectively. This confirms the favorability of the experimental conditions used in this sorption [18].

The values of 769.23, 909.09, 1111.11 and 1250.00 mg g⁻¹ (table 5) are the maximum capacities for MnO₄⁻ anions sorption by CuS at temperatures of 20 °C, 30 °C, 40 °C, and 60 °C correspondingly. In comparison between the high sorption capacities obtained in this research and the sorption capacities of the other sorbent have been used before this work for elimination of MnO₄⁻ anions from aqueous solutions (table 6), it will be found that CuS due to its higher surface area (798.91 m²g⁻¹) and its higher chemical activity is the best sorbent has been applied for sorption the anions of MnO₄⁻ from aqueous media till now. Moreover, these sorption capacities can be higher if the adsorption processes carried out at solution pH of 1.5. Thus, CuS will get special considerations in the processes of water and wastewaters decontaminations.
Table 5. Isotherm constants of $\text{MnO}_4^-$ anions sorption by CuS nanoparticles.

| Temperature | $q_{\text{max}}$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) | $R_L$ | $R^2$ | $K_L$ (mg g$^{-1}$) | $1/n$ | $n$ | $R^2$ | $K_T$ (L mg$^{-1}$) | $B_T$ | $R^2$ |
|-------------|-------------------------------|---------------------|-------|-------|---------------------|-------|-----|-------|---------------------|-------|-------|
| 20 °C       | 769.23                        | 0.0057              | 0.1052| 0.997 | 138.56              | 0.227 | 4.415| 0.938 | 0.06                | 158.78 | 0.992 |
| 30 °C       | 909.09                        | 0.0112              | 0.0564| 0.996 | 111.87              | 0.310 | 3.229| 0.969 | 0.15                | 176.51 | 0.976 |
| 40 °C       | 1111.11                       | 0.0459              | 0.0143| 0.990 | 419.60              | 0.142 | 7.022| 0.882 | 0.37                | 97.67  | 0.823 |
| 60 °C       | 1250.00                       | 4.0000              | 0.0002| 1.000 | 698.76              | 0.114 | 8.757| 0.437 | 1847.93             | 98.88  | 0.519 |
3.2.5. Thermodynamic outcomes

The values of ln\(\frac{q_e}{C_0}\) were plotted against the 1/T (K\(^{-1}\)) values (figure 14) for sorption of 1300, 1400, 1500 mg l\(^{-1}\) of \(\text{MnO}_4^-\) solutions by the sorbent of CuS. The values of \(\Delta H^\circ\) and \(\Delta S^\circ\) listed in table 7 were calculated from the slopes and intercepts of the plots of figure 14. The calculated values of these two parameters (\(\Delta H^\circ\), \(\Delta S^\circ\)) were used for computing \(\Delta G^\circ\) values using equation (7). The positive values of \(\Delta S^\circ\) (table 7) approve that the randomness between CuS (solid phase) and sorbate solution (liquid phase) at the interface decreased due to the sorption process [30]. Furthermore, the \(\Delta S^\circ\) value is decreased from 0.1947 to 0.1371 by augmenting the concentration of \(\text{MnO}_4^-\) solution in the rage of 1300–1500 mg l\(^{-1}\). This shows, that the performance of this sorption is strongly influenced by the initial concentration of \(\text{MnO}_4^-\) solution. Whereas, the \(\Delta H^\circ\) positive values (table 7) confirm that sorption of \(\text{MnO}_4^-\) anions by CuS is a heat-absorbing process [31]. Additionally, all values of \(\Delta H^\circ\) are higher than 20.9 KJ mol\(^{-1}\), which means that the anions of \(\text{MnO}_4^-\) were chemically adsorbed on the surface of CuS [32]. It can also be noted from table 7, that \(\Delta G^\circ\) parameter has positive values 20 °C and negative values at the other three higher temperature. This designates that this sorption is a non-spontaneous and

![Figure 14. The relationship between ln\(\frac{q_e}{C_0}\) and 1/T for \(\text{MnO}_4^-\) sorption by CuS nanoparticles.](image)

**Table 6.** The sorption capacities of \(\text{MnO}_4^-\) anions by various sorbents.

| Adsorbents                              | \(q_{\text{max}}\) (mg g\(^{-1}\)) | Sources          |
|----------------------------------------|------------------------------------|------------------|
| CuS nanoparticles                      | 769.23                             | 20 °C This study |
|                                        | 909.09                             | 30 °C            |
|                                        | 1111.11                            | 40 °C            |
|                                        | 1250.00                            | 60 °C            |
| Modified powder of Sage leaves         | 714.29                             | 30 °C [12]       |
|                                        | 769.23                             | 40 °C            |
|                                        | 833.33                             | 50 °C            |
|                                        | 909.09                             | 60 °C            |
| Modified powder of Nitraria retusa leaves | 312.50                            | 30 °C [10]       |
|                                        | 333.33                             | 50 °C            |
|                                        | 344.83                             | 60 °C            |
| Activated carbonaceous materials       | 100.00 ± 0.5%                      | [21]             |
| Activated carbon produced from animal bone | 28.04                             | [9]              |
| Activated carbon produced from corn cob | 26.00                             | [9]              |
| Activated Charcoal                     | 57.47                              | [2]              |
| Activated carbon derived from shells of coconut | 23.25                             | [8]              |

**Table 7.** Thermodynamic constants of \(\text{MnO}_4^-\) anions sorption by CuS nanoparticles.

| Initial concentration (mg l\(^{-1}\)) | \(\Delta H^\circ\) (KJ mol\(^{-1}\)) | \(\Delta S^\circ\) (KJ mol\(^{-1}\)) | \(\Delta G^\circ\) (KJ mol\(^{-1}\)) |
|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
|                                      | 293K                                 | 303K                                 | 313K                                 | 333K                                 | R\(^2\)       |
| 1300                                 | 57.589                               | 0.1947                               | 0.54312                              | 1.40385                              | 3.35082      | 7.24477 | 0.995 |
| 1400                                 | 48.309                               | 0.1625                               | 0.696838                             | 0.92813                              | 2.5531       | 5.80305 | 0.993 |
| 1500                                 | 41.048                               | 0.1371                               | 0.885516                             | 0.48521                              | 1.85594      | 4.5974  | 0.992 |
spontaneous process at low and high temperatures, respectively. Table 7 also reveals that the ΔG° values become more negative by rising temperature. This indicates that the temperature has a significant and vital role in this sorption.

4. Conclusions

CuS powder was characterized and utilized as sorbent for removing of MnO₄⁻ anions from aqueous media. The influences of the most important experimental conditions such as the sorbent dosage, MnO₄⁻ initial concentration, solution pH, sorption contact time and temperature on the efficiency of this sorption were studied. It was found that the capacity of this sorption is positively influenced by increasing the sorbent dose, initial concentration of MnO₄⁻ and sorption contact time in the ranges of (0.005–0.02 g), (400–1200 mg l⁻¹) and (0–90 min), respectively. The sorption capacity almost was constant in the cases of sorbate initial concentrations, agitation time and sorbent dosage over 1200 mg l⁻¹, 90 min and 0.02 g, correspondingly. Moreover, the sorption in this work was negatively influenced by solution pH and positively affected by temperature. The parameters of this sorption kinetic were determined for three kinetic models and the obtained data confirmed that the model of 2nd order was the best. Three isotherm models were also utilized for describing the equilibrium data and the outcomes proved that Langmuir model was the best model can be applied for describing the equilibrium data of this sorption. Additionally, thermodynamic constants of this sorption were investigated. The results attained in this research suggest that sorption of MnO₄⁻ anions by CuS is an endothermic, monolayer and spontaneous sorption, chemisorption and CuS has homogeneous effective sites. The sorption capacities of 769.23, 909.09, 1111.11 and 1250 mg g⁻¹ were obtained at 20°C, 30°C, 40°C and 60°C, respectively. These high capacities confirm that CuS will get a great attention in the field of water and wastewater purifications from the anions of MnO₄⁻.

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