Nonlinear regression for analysis of the uptake of KMnO4 from aqueous solutions onto natural marl

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Abstract. The present work aims to evaluate the performance of raw marl collected from the region of Oum El Bouaghi on the elimination of KMnO4 from aqueous solution. The adsorption capacities were studied using the batch technique as a function of pH, initial concentration and temperature. The maximum adsorption for KMnO4 was found to be 83.517% at pH 3.0. When the pH is low (pH<3.0), the uptake of KMnO4 occurs with an electrostatic attraction between the MnO4- ions and the surface proton groups, while at pH ≥3.0-8.0, the formation of complexes with the surface functional groups during the adsorption process and/or cation exchange are responsible for retention of Mn(II) ions onto marl. Experimental adsorption data were modeled with different nonlinear isotherms and kinetic models. Furthermore, statistical errors (SSE, SD, ARE, $\chi^2$, $R^2$ and $R^2_{adj}$) were calculated to choose the suitable model. Langmuir isotherm was found to be best for fitting the experimental data. The calculated thermodynamic parameters indicate that adsorption process was physical, spontaneous and endothermic in nature. From this work, it was concluded that the natural marl can be used for effective elimination of KMnO4 from aqueous solution and wastewater.

1. Introduction
Manganese is the second most abundant heavy metal in nature. It is used in the manufacture of iron and steel alloys, glass, welding works, fireworks, dry battery cells, electric coils and pesticides [1-3]. Manganese can exist in aqueous solutions with different oxidation states (II to VII). The water soluble forms are Mn(II) and Mn(VII) [4]. Manganese is considered as an essential micronutrient for organisms and plants. When manganese concentrations exceed 0.1 mg.L$^{-1}$ in water bodies, dissolved oxygen is reduced, giving off an undesirable taste that can affect the central nervous system of living organisms [5, 1]. Due to the harmful effects of manganese, its ions removal from wastewater and industrial effluents is crucial. Among the physico-chemical water treatment processes, the adsorption method is commonly used because it is efficient, simple, selective and inexpensive. Recently, the search for new, efficient, inexpensive and eco-friendly adsorbents is gaining an increasing interest by researchers. Regarding Marl, it is a sedimentary rock composed of a mixture of clay and carbonate [6]. However, the data available on the adsorption of toxic metals on this type of material is limited. The aim of this study, thus, is to assess the feasibility of using raw marl from the Oum El Bouaghi region as a new natural adsorbent to remove MnO4- from the aqueous solution. The study of the reaction parameters (initial concentration, pH and temperature) and the adsorption isotherms were carried out in a batch
system. Modeling of adsorption isotherms was estimated using nonlinear regression. The best models are selected after analyzing the errors. The thermodynamics of adsorption were also carried out in this work.

2. Experimental

The adsorbent used is marl taken from the R’ghiss Mountain located in the region of Oum El Bouaghi (Algeria). It is collected, washed with distilled water, dried in the open air and sieved through a 180 μm sieve. Mineralogical analysis has shown that this solid is composed of 15% quartz, 17% calcite, 05% albite, 23% illite, 13% kaolinite, 20% montmorillonite and 07% ferruginous minerals + others. Its specific surface determined by the BET method is 14.603 m².g⁻¹ [7]. The stock solution of MnO₄⁻ with a concentration of 200 mg.L⁻¹ was prepared by dissolving potassium permanganate (KMnO₄, M = 158.04 g.mol⁻¹, purity: 99%, Merck) in distilled water. The solutions at different concentrations used in our study were obtained by diluting the stock solution. The pH of the solution is adjusted by adding 0.1 M HCl or 0.1 M NaOH solutions. The pH value of the solution was measured by a Jenway model pH meter. The adsorption experiments were carried out by the batch method by bringing 25mL of different experimental solutions of MnO₄⁻ into contact with 0.4g of marl in 500ml conical flasks. The effects of initial adsorbate concentration (4–10 mg.L⁻¹), pH (2.0–8.0) and temperature (293–303K) on manganese ion retention by marl were investigated. The samples were stirred at a speed of 475 rpm in a water bath shaker (Heizung model) for a known period of time. Then the mixtures were centrifuged at 3500 rpm for 5 min in a Hettich Universal centrifuge. The supernatants were collected and analyzed by molecular absorption spectrophotometry (Spectronic 70 spectrophotometer). The residual concentration of manganese in aqueous solution was determined by referring to the calibration curve obtained from the test solutions at the wavelength λmax = 525 nm (figure 1). The percentage of removal (R%) of manganese ions was calculated by equation (1):

\[ R(\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \tag{1} \]

where:

C₀ (mg.L⁻¹) and Cₜ (mg.L⁻¹) are the initial and residual concentrations of MnO₄⁻.

![Figure 1. Calibration curve for the KMnO₄ solution.](image_url)
2.1. Statistical analysis
In our work, the fitting of the experimental data to the isothermal models was performed according to the nonlinear regression using the Origin 9.0 software. Nonlinear regression is the best method to determine the parameters of isotherms [8]. Six different error functions (SSE, SD, \(\chi^2\), ARE, \(R^2\), and \(R^2_{adj}\)) were analyzed to examine the validity of mathematical models and predict the best models. The error functions are presented by the following equations:

- **The Sum of Squared Errors (SSE)**
  \[
  \text{SSE} = \sum_{i=1}^{N} (q_{t,\text{cal}} - q_{t,\text{exp}})^2 
  \]

- **Standard deviation (SD)**
  \[
  \text{SD} = \left( \frac{1}{N-P} \sum_{i=1}^{N} (q_{t,\text{cal}} - q_{t,\text{exp}})^2 \right)^{1/2} 
  \]

- **Chi-square test \(\chi^2\)**
  \[
  \chi^2 = \frac{1}{N-P} \sum_{i=1}^{N} \frac{(q_{t,\text{exp}} - q_{t,\text{cal}})^2}{q_{t,\text{cal}}} 
  \]

- **Average relative error (ARE)**
  \[
  \text{ARE} = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{q_{t,\text{cal}} - q_{t,\text{exp}}}{q_{t,\text{exp}}} \right| 
  \]

- **Coefficient of determination \(R^2\)**
  \[
  R^2 = \frac{\left( q_{t,\text{exp}} - \bar{q}_{t,\text{cal}} \right)^2}{\sum_{i=1}^{N} (q_{t,\text{exp}} - q_{t,\text{cal}})^2 + (q_{t,\text{exp}} - \bar{q}_{t,\text{exp}})^2} 
  \]

- **Adjusted R-squared \(R^2_{adj}\)**
  \[
  R^2_{adj} = 1 - \frac{(N-1)(1-R^2)}{(N-P)} 
  \]

where:
- \(q_{t,\text{cal}}\) (mg g\(^{-1}\)) and \(q_{t,\text{exp}}\) (mg g\(^{-1}\)) are the calculated and experimental adsorption amounts respectively,
- \(\bar{q}_{t,\text{cal}}\) (mg g\(^{-1}\)) refers to the average of the calculated adsorbed amount,
- \(N\) is the number of experimental data points,
- \(P\) is the number of parameters of the fitted model.

The experimental results agree with the theoretical models when the values of \(\text{SSE}, \chi^2, \text{SD}, \text{ARE}\) tend towards 0, and the coefficients \(R^2\) and \(R^2_{adj}\) tend towards 1.

3. Results and Discussion

3.1. Effect of the initial concentration
The effect of the initial concentration on the adsorption efficiency was studied. The experimental data are represented graphically in figure 2. The retention of manganese increases strongly in the initial stages and then gradually to reach equilibrium after 180 min of the contact time. The increase in the initial
KMnO₄ concentration from 4 mg.L⁻¹ to 10 mg.L⁻¹ leads to an increase in the amount adsorbed from 40.539% to 83.517%. This behavior can be explained by the increase in the driving force which overcomes the various mass transfer resistances of metal ions from the aqueous phase to the solid phase. Consequently, the number of collisions between the MnO₄⁻ ions and the active sites of the adsorbent increases, this leads to the increase of the adsorbed quantity.

![Figure 2](image)

**Figure 2.** Effect of the initial concentration of MnO₄⁻ (pH=3.0, T=293K, v=475 rpm, m=0.4g).

3.2. **Effect of pH**

Adsorption is highly dependent on pH of the aqueous solution since it is attributed to distribution of different adsorbed species in the medium as well as the surface charge and degree of adsorbent ionization [9]. Manganese adsorption was carried out in acidic, neutral and basic medium in the pH range 2 to 8 as shown in figure 3. In medium of high acidity, KMnO₄ produces manganese (II). On the other hand, KMnO₄ produces manganese dioxides under acid-neutral and alkaline pH conditions, as illustrated by equations (8), (9), and (10) [10].

In a strong acidity medium:

\[
\text{MnO}_4^- + 8H^+ + 5\varepsilon \rightarrow \text{Mn}^{2+} + 4H_2O, \quad (E^o = +1.51V)
\]  

(8)

In an acid-neutral medium:

\[
\text{MnO}_4^- + 4H^+ + 3\varepsilon \rightarrow \text{MnO}_2(s) + 2H_2O, \quad (E^o = +1.70V)
\]

(9)

In alkaline medium:

\[
\text{MnO}_4^- + 2H_2O + 3\varepsilon \rightarrow \text{MnO}_2(s) + 4OH^-, \quad (E^o = +0.59V)
\]

(10)
Figure 3. Effect of pH on the adsorption of KMnO$_4$ by marl ($C_0=10$ mg L$^{-1}$, $T=293K$, $v=475$ rpm, $m=0.4g$).

The results clearly show that the percentage of manganese extraction in aqueous solution increases up to pH 3.0 (83.517%). In this case, the elimination of KMnO$_4$ by the marl refers to the electrostatic attraction between the MnO$_4^-$ ions and the protonated groups of the surface involving the formation of an ion pairing and favoring the elimination of Mn$^{7+}$ in aqueous solution. In addition, we can also observe that the removal rate of manganese decrease from 83.517% to 70.131% as pH rises above 3.0 due to the increase of the electrostatic repulsion forces between the MnO$_4^-$ and the active sites on the surface which reduces the elimination of Mn$^{7+}$. The deprotonating of the surface decreases the competition between the H$^+$ ions and the Mn$^{2+}$ ions leading to a decrease in electrostatic repulsions. Manganese (II) ions resulting from the reduction of MnO$_4^-$ are adsorbed by the marl through the formation of complexes with active surface functional groups (OH) and/or by cation exchange with cations located in exchangeable sites of clay [12]. The maximum adsorption of Mn$^{2+}$/7+ ions was found at pH 3.0 and therefore the optimum pH value is 3.0.

3.3. Effect of Temperature
The study of the evolution of MnO$_4^-$ elimination was carried out at different temperatures: 293K, 298K, 303K (figure 4). We perceive an increase in Mn$^{3+/7+}$ ion extraction from 83.51667% to 88.38404% with increasing temperature, revealing the endothermic nature of adsorption. In contrast, the increase in adsorption capacity can be attributed to the acquisition of additional kinetic energy to facilitate the diffusion and removal of Mn.
3.4. Adsorption Isotherms

In our study, the experimental data corresponding to the equilibrium are analyzed in the temperature range 293K to 303K at pH=3.0 by isotherms models Langmuir (equation (11)) [13] and Freundlich (equation (12)) [14].

\[ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \]  

(11)

\[ q_e = K_F C_e^{\frac{1}{n}} \]  

(12)

where:

- \( K_L \) (L.mg\(^{-1}\)) is the equilibrium constant of Langmuir isotherm, \( q_m \) (mg.g\(^{-1}\)) is the maximum adsorption amount of the solute on the solid phase, \( q_e \) is the amount of adsorbed of the solute on the solid phase at equilibrium (mg.g\(^{-1}\)), \( C_e \) (mg.L\(^{-1}\)) is the concentration of the metal in the solution at equilibrium, \( K_F \) is the constant of the Freundlich isotherm, \( n \) expresses the adsorption intensity (without units).

Table 1 represents the various parameters calculated from the graphic representation of these two models. A slight improvement in manganese adsorption was found with increasing temperature, which shows that the adsorption process is endothermic. Similar results are found by Kebabi et al (2017) [15]. The Freundlich parameter values (n) (1.894≤n≤2.459) indicate that the adsorption of Mn on the marl is favorable, the exponent n gives an indication of the adsorption favorability. The values of \( K_L \) and \( q_m \) increase with the rise of temperature, which means that the affinity between manganese ions and marl develops with increasing temperature and the adsorption of Mn\(^{2+/7+}\)ions on the marl has an endothermic nature. Note that, the Langmuir isotherm model gives the best fit of the experimental data with values of \( R^2 \) and \( R^2_{adj} \) closer to unity and of order greater than 0.98. The values of SSE, SD, \( \chi^2 \), ARE corresponding to the Langmuir isotherm are lower than those obtained by the Freundlich isotherm. This result is consistent with other works in the literature [16-19].
Table 1. Parameters of ion adsorption isotherms of Mn\(^{2+/7+}\) on marl.

| Isotherm | Parameter | \(T\) (K) | \(q_m\) (mg.g\(^{-1}\)) | \(K_L\) (L.mg\(^{-1}\)) | \(SSE\) \(10^4\) | \(SD\) | \(\chi^2\) \(10^4\) | \(\text{ARE}\) | \(R^2\) | \(R^2_{adj}\) |
|----------|-----------|-----------|----------------|----------------|----------------|-------|----------------|---------|--------|----------|
|          |           | 293       | 298           | 303           |                |       |                |         |        |          |
| Langmuir |           |           |                |                |                |       |                |         |        |          |
|          |           | 0.512     | 0.55           | 0.585         | 8.92.10\(^4\) | 0.014 | 31.5.10\(^4\) | 4.58    | 0.99   | 0.987    |
|          |           | 0.903     | 0.974          | 1.103         | 5.54.10\(^4\) | 0.012 | 18.2.10\(^4\) | 3.33    | 0.994  | 0.993    |
|          |           | 1.103     |                |              | 2.716.10\(^4\) | 0.008 | 7.904.10\(^4\) | 1.835   | 0.997  | 0.997    |
| Freundlich |       |           |                |                |                |       |                |         |        |          |
|          |           | 0.243     | 0.268          | 0.3           | 15.7.10\(^4\) | 0.018 | 55.5.10\(^4\) | 0.43    | 0.023  | 0.021    |
|          |           | 0.407     | 0.421          | 0.43          | 12.8.10\(^4\) | 0.018 | 42.7.10\(^4\) | 2.459   | 0.912  | 0.919    |
|          |           | 0.268     |                |              | 10.3.10\(^4\) |       | 32.2.10\(^4\) | 2.374   | 0.939  | 0.944    |

3.5. Thermodynamic study

Thermodynamic parameters such as Gibbs free energy change (\(\Delta G^0\)), enthalpy change (\(\Delta H^0\)) and entropy change (\(\Delta S^0\)) are calculated from the following equations [20]:

\[
\Delta G^0 = -RT \ln(K^0_e) \quad (13)
\]

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (14)
\]

\[
\ln(K^0_e) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \frac{1}{T} \quad (15)
\]

where:

\(K^0_e\) is the thermodynamic equilibrium constant (dimensionless).

The slope and the intercept of a graph of \(\ln(K^0_e)\) vs \((1/T)\) are used to determine the values of \(\Delta H^0\) and \(\Delta S^0\) respectively (figure 5). The results are collated in table 2.

The results reveal the decrease in \(\Delta G^0\) from -28.244 to -29.714 kJ.mol\(^{-1}\), these negative values indicate the feasibility and spontaneity of the adsorption process of Mn\(^{2+/7+}\) ions. The positive value of \(\Delta H^0\) (14.806 kJ.mol\(^{-1}\)) shows that the adsorption process is physical and endothermic in nature. The positive value of \(\Delta S^0\) (146.857 J.K\(^{-1}\).mol\(^{-1}\)) provides evidence that the adsorption process has increasing random behavior at the solid - solution interface.
Figure 5. Representation of the variation of \( \ln(K^e) \) as a function of \( 1/T \).

Table 2. Thermodynamic parameters of adsorption of Mn\(_{2+/7+}\) by marl.

| T(K) | \( \Delta G^\circ \) (kJ.mol\(^{-1}\)) | \( \Delta S^\circ \) (J.K\(^{-1}\).mol\(^{-1}\)) | \( \Delta H^\circ \) (kJ.mol\(^{-1}\)) | \( R^2_{adj} \) |
|------|-------------------------------|---------------------|----------------------|-------------------|
| 293  | -28.244                        |                     |                      |                   |
| 298  | -28.915                        | 146.857             | 14.806               | 0.957             |
| 303  | -29.714                        |                     |                      |                   |

4. Conclusion

In this study, marl of Oum El Bouaghi region was used as an adsorbent to remove MnO\(_4^-\) from the aqueous solution. The main results are as follows:

- The initial concentration and temperature have positively influence the removal of Mn\(_{2+/7+}\) ions.
- The adsorption process reaches equilibrium after 180 minutes.
- Maximum removal of Mn was found at pH = 3.0. When the pH is below 3.0, the percentage of extraction of manganese in aqueous solution increases. The electrostatic attraction between the MnO\(_4^-\) ions and the proton groups on the surface. When the pH is above 3.0, the increase in electrostatic repulsive forces between MnO\(_4^-\) ions and active sites on the surface decreases the removal of Mn\(_{7+}\) ions. Mn\(_{2+}\) ions can be adsorbed on the marl by the formation of complexes with the active surface functional groups (OH) of the complexes and/or by cation exchange with the cations located in the exchangeable sites of the clay.
- The equilibrium data were well fitted by the Langmuir isotherm.
- The thermodynamic study shows that the adsorption process is physical, endothermic, and spontaneous.
The results of this study support the use of Oum El Bouaghi marl to effectively remove KMnO₄ from wastewater.

References
[1] Mahadevaiah N, Vijayakumar B, Hemalatha K and Prakash B J 2011 Bull. Mater. Sci. 34 1675
[2] Winder C 2004 Toxicity of metals Occupational Toxicology vol 2, ed C Winder and N H Stacey (Boca Raton: CRC Press) chapter 12 p 298
[3] Nieva A D, Doma B T and Chao H P 2018 IOP Conf. Ser.: Earth Environ. Sci. 191 012034
[4] Patil D S, Chavan S M and Oubagarunadin J U K 2016 J. Environ. Chem. Eng. 4 468
[5] Chen F, Hong M, You W, Li C and Yu Y 2015 Appl. Surf. Sci. 357 856
[6] Cornell R M and Aksoyoglu E S 1991 Clay. Miner. 26 567
[7] Bouzeghaia E A, Hafsi S, Gherraif N 2018 World. J. Environ. Biosci. 7 8
[8] Jasper E E, Ajibola V O and Onwuka J C 2020 Appl. Water. Sci. 10 1
[9] Anirudhan T S, Nima J and Divya P L 2013 Appl. Surf. Sci. 279 441
[10] Liu R, Liu H, Zhao X, Qu J and Zhang R 2010 J. Hazard. Mater. 176 926
[11] Mahmoud M E, Yakout A A, Saad S R, and Osman M M 2016 Desalination. Water. Treat. 57 15559
[12] Eba F, Gueu S, Eya’A-Mvongbote A, Ondo J A, Yao B K, Ndong N J and Kouya B R 2010 Int. J. Eng. Sci. Technol. 2 5001
[13] Langmuir I 1918 J. Am. Chem. Soc. 40 1361
[14] Freundlich H 1906 J. Phys. Chem. 57 385
[15] Kebabi B, Terchi S, Bougherara H, Reinert L and Duclaux L 2017 Appl. Clay. Sci. 139 92
[16] Taffarel S R and Rubio J 2009 Miner. Eng. 22 336
[17] Kocaoba S 2009 Desalination. 244 24
[18] Al-Aoh H A 2019 Mater. Res. Express. 6 115102
[19] Alcaraz L, Aiguacil F J and López F A 2021 Can. J. Chem. Eng. 99 447
[20] Lima E C, Hosseini-Bandegharaei A, Moreno-Piraján J C and Anastopoulos I 2019 J. Mol. Liq. 273 425