Potassium permanganate dye removal from synthetic wastewater using a novel, low-cost adsorbent, modified from the powder of *Foeniculum vulgare* seeds

Suhair. A. Bani-Atta

In this study, Seeds powder of *Foeniculum vulgare* was used to prepare a novel adsorbent, the modification of the prepared adsorbent was done by each of ZnCl₂, oxalic acid, and CuS, all samples have been characterized by different techniques and examined for Potassium permanganate (KMnO₄) adsorption. Among the four modified and unmodified adsorbents, the sample modified by oxalic acid has the highest percentage removal for KMnO₄ adsorption (%R = 89.36). The impact of KMnO₄ concentration, adsorbent dose, contact temperature, contact time, and solution pH on the adsorption performance was also investigated. The experimental data of this adsorption was analyzed by different kinetic and isotherm models. As Constants of thermodynamic ΔG°, ΔH°, and ΔS° have been also evaluated. Surface area, pore volume, and pore size of the modified oxalic acid *F. vulgare* seeds powder adsorbent were determined as 0.6806 m² g⁻¹, 0.00215 cm³ g⁻¹, and 522.063 Å, as pHₚₑₙ was also stated to be 7.2. The R² values obtained from applying different isotherm and kinetic models (0.999 and 0.996) showed that the adsorption performance of KMnO₄ follows the Langmuir and Pseudo 2nd order models. Furthermore, high adsorption capacities of 1111.11, 1250.00, and 1428.57 mg g⁻¹ were achieved at three temperatures that were used in this study. Constants of thermodynamic ΔG°, ΔH°, and ΔS° values indicate chemical and spontaneous adsorption at the adsorbent surface. Therefore, the modified adsorbent can be used to remove KMnO₄ dye from pollutant water samples.

Potassium permanganate (KMnO₄) is a highly strong oxidizing agent that is commonly used for water purification from numerous pollutants, mainly for the destruction of compounds that cause undesirable taste, odor, and color for the treated water. Remarkably, permanganate is still one of the most oxidizing chemicals ever applied to remove each iron, manganese, and arsenic from water. In addition to its great ability to oxidize cyanide, phenols, and organic compounds. Recently, many studies reported that excessive exposure to KMnO₄ may cause acute problems of the nervous system, irritation of the skin and eye. Furthermore, it was stated that manganese has significant toxicity towards the liver and kidneys. Therefore many techniques and methods have been applied for KMnO₄ removal from the contaminated water. For instance, fluidized-bed crystallization method was used, concerning the ease of preparation and use, in addition to the high capacity to get rid of permanganate from wastewater adsorption is one of the most extensively utilized processes with different adsorbents, activated carbon is a common adsorbent that used for adsorption of KMnO₄ from polluted water due to its high adsorption efficiency. To remove KMnO₄, molecules from polluted aqueous solutions by adsorption a lot of activated carbon adsorbents were prepared using shells of coconut, corn cob, and animal bone were also applied, sulfuric acid modification of activated carbon, and activated charcoal have been used too. More recently, Nanoparticles of metallic oxides have been used to remediate effluent from various dyes. Copper sulfide nanoparticles were used as dynamic adsorbents to treat the synthetic wastewater from potassium permanganate ions. Despite the great performance and significant efficiency of activated carbon and metallic oxides Nanoparticles, its requirements and conditions of preparation are rather difficult and expensive. Thus, prompted the researchers...
to use low-cost materials within their areas and applied them as adsorbents for permanganate ions adsorption. For instance, sage\textsuperscript{22}, Neem\textsuperscript{22}, Nitraria retusa\textsuperscript{23}, and Ocimum basilicum\textsuperscript{23} were used as low-cost sorbents to remove Permanganate anions from synthetic samples.

Foeniculum vulgare plant is well-known by fennel in many countries as shamr in Saudi Arabia, mainly used as food and tea flavored and considered as a flavored spice, its seeds were used as antitumor\textsuperscript{24}, antimicrobial\textsuperscript{25}, and antioxidant\textsuperscript{26}. Experiments on animals and clinical trials recommend that chronic use of \textit{F. vulgare} plant is not harmful and no toxicity marks were detected\textsuperscript{27}.

Gold nanoparticles based on seeds extract of fennel \textit{E. vulgare} plant was synthesized and its catalytic activity against rhodamine B and methylene blue days were examined\textsuperscript{28}, \(V_2O_5–Fe_2O_3\) nanocomposites from stem powder of \textit{E. vulgare} have been also produced and the catalytic performance of nanocomposites particles was assessed for reduction of 4-nitrophenol\textsuperscript{29}.

Up to now, no adsorbent based on \textit{F. vulgare} seeds was prepared in any form and applied to eliminate the hazardous dyes from water even permanganate ions, despite the excellent medical properties of this herb, in addition to its widespread over the world \textit{F. vulgare} seeds are considered a low-cost material. Therefore, this research mainly aimed to prepare a new adsorbent from seeds of \textit{F. vulgare} and to investigate the adsorbent performance toward eliminating KMnO\textsubscript{4} from polluted water. Thermodynamics, Kinetics, and isotherms parameters will also be studied. The performance of this adsorption will be also studied through conditions and impacts that could affect on KMnO\textsubscript{4} removal experiment, as the adsorption capacity of modified adsorbent for removal of KMnO\textsubscript{4} will be critically addressed.

To achieve all the desired goals of this work and get the best results, unmodified samples from \textit{F. vulgare} seeds have been synthesized and the modification has been also carried out by zinc chloride, copper sulfide, and oxalic acid; both types of samples have been characterized and examined as adsorbents for KMnO\textsubscript{4} removal from water, to choose the best adsorbent, the adsorption performances have been compared, then all the KMnO\textsubscript{4} adsorption experimental factors and conditions of selected adsorbent were tested.

Materials and methods

Materials. \textit{Foeniculum vulgare} seeds were obtained from a local market in Tabuk City, KSA. All chemicals that were used in this work were obtained from Sigma-Aldrich with a purity of (37\%) for hydrochloric acid, ≥ 97\% for sodium hydroxide ≥ 97\% for zinc chloride, ≥ 99.99\% for oxalic acid, ≥ 99-99\% for copper sulfide, and ≥ 99.00\% for sodium carbonate.

Preparation and modification of adsorbents. The \textit{F. vulgare} seeds were washed with distilled water several times and then dried overnight, after that, the \textit{F. vulgare} seeds powder (FVESP) was obtained by an electric grinder. A sample of 100 g was refuxed for 180 min with 1 L of oxalic acid (20\% w/w), afterwards, the mixture was allowed to cool at room temperature. The solid part was separated by filtration, to get rid of any excess amount of oxalic acid; the solid was heated for 90 min with 250 mL of 2 M hydrochloric acid. Then, the filtration of the new mixture was done many times and rinsed with distilled water to have a clean solid, to get rid of any water present in the sample; the solid was left in the oven for 30 h at 130 °C. Finally, to ensure the homogeneity of the sample, the dry solid was grounded and sieved, and the resulted adsorbent of oxalic acid \textit{F. vulgare} seeds powder labeled as (Ox-FVESP).

The same procedure was repeated with mixtures containing 100 g of FVESP with 1 L of 20\% w/w acidic solution of zinc chloride, and 100 g FVESP with a mixture of 20\% w/w acidic solution of zinc chloride and 50 g of copper sulfide. The resulted adsorbents of zinc chloride \textit{F. vulgare} seeds powder labeled as (Zn-FVESP), and zinc chloride/copper sulfide \textit{F. vulgare} seeds powder labeled (Zn/Cu-FVESP).

Characterization of FVESP adsorbents. To recognize the surface morphology of the modified and unmodified FVESP adsorbents SEM instrument was used at a 10 kV accelerating voltage. And to determine the surface adsorbents’ functional groups, the FT-IR instrument (Nicolet iS5 of Thermo Scientific FT-IR, USA) was used. The surface area and porosity of each adsorbent were estimated using BET (NOVA-2200 Ver. 6.11) technology for 22 h and 77.35 K. In addition, 40 mL of 0.05 M Na\textsubscript{2}CO\textsubscript{3} solutions varying with 2, 4, 6, 8, and 10 initial values of pH\textsubscript{i} have been mixed in a 150 mL plastic container with 0.2 g of the idealistic adsorbent. After shaking all containers for 26 h 175 rpm and 27 °C conditions in a shaker incubator, filtration of each was done, then using a pH meter, the final pH of each solution was determined. Finally, to determine the pH\textsubscript{ZPC} value of this adsorbent, the values of (pH\textsubscript{i} − pH\textsubscript{f}) have been calculated and graphed against the pH\textsubscript{i} values.

Adsorption experiments. The idealistic adsorbent identification. To determine the superlative as well as the most efficient adsorbent developed in the current study for KMnO\textsubscript{4} removal from synthetic aqueous samples, 20 mL of 100 mg L\textsuperscript{-1} KMnO\textsubscript{4} solution concentration was combined with 0.03 g of FVESP in a 30 mL amber bottle. A shaker incubator was used for 30 h to stir the sealed amber bottle at 27 °C and 180 rpm. After that, the mixture was filtered; The Jenway UV-6800 UV–Vis spectrophotometer was used at 525 nm to measure the balanced concentration of KMnO\textsubscript{4} in the filtrate. The same procedure was repeated with Ox-FVESP, Zn-FVESP, and Zn/Cu-FVESP adsorbents for the KMnO\textsubscript{4} adsorption. Equations (1) and (2) were used to calculate the KMnO\textsubscript{4} percentage removal percent %R and the quantities of KMnO\textsubscript{4} adsorbed at equilibrium Q\textsubscript{e} mg g\textsuperscript{-1} by both modified and unmodified adsorbents.

\[
\%R = \frac{C - C_f}{C} \times 100\%
\]  
(1)
where \( C_\circ \) is the KMnO\(_4\) initial concentration and \( C_e \) is the KMnO\(_4\) final concentration, \( m \), and \( V \) are the mass of adsorbent (g), and KMnO\(_4\) solution volume (L), respectively.

**Experimental conditions impact.** Batch experiments have been conducted to observe and identify the most significant factors that affect KMnO\(_4\) adsorption experiments by ideal adsorbent Ox-FVES, such as concentration of KMnO\(_4\) (10–1400 mg L\(^{-1}\)), contact time (0–320 min), the dosage of Ox-FVES adsorbent (0.005–0.035 g), the adsorption temperature (27–57 °C), and the pH (1.5–11.5). All of the Batch experiments have been done in 30 mL amber bottles by adding 20 mL of KMnO\(_4\) solution to enough amounts from Ox-FVES. A shaker incubator at 180 rpm was used to shake all sealed amber bottles for a required time, followed by filtration of each mixture, and the remaining concentrations of KMnO\(_4\) were measured as mentioned previously.

To compute the adsorbed amount of KMnO\(_4\) at equilibrium \((Q_e, \text{mg g}^{-1})\) by the Ox-FVES adsorbent and time \(t (Q_t, \text{mg g}^{-1})\) Eqs. (2) and (3) were applied:

\[
Q_e = \frac{V}{m} (C_\circ - C_e)
\]  

(2)

\[
Q_t = \frac{V}{m} (C_\circ - C_t)
\]  

(3)

where \( C_t \) (mg L\(^{-1}\)) is the KMnO\(_4\) concentration at contact time.

**Temperature impact and isotherm studies.** The outcomes obtained from the Batch experiments for 10–1400 mg L\(^{-1}\) KMnO\(_4\) solutions by 0.02 g by Ox-FVES adsorbent at 26 h contact time and three different temperatures (27, 42, and 57 °C) and 190 rpm have been analyzed according to the three isotherm models, Langmuir, Freundlich, and Temkin linear forms, Eqs. (4–6) respectively. The parameter of equilibrium \( R_L \) value of the Langmuir isotherm model was also evaluated according to Eq. (7).

\[
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}} K_L} + \frac{C_e}{q_{\text{max}}}
\]  

(4)

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

(5)

\[
q_e = B_1 \ln K_T + B_1 \ln C_e
\]  

(6)

\[
R_L = \frac{1}{1 + K_L C_0}
\]  

(7)

where \( C_0 \) is the maximum initial concentration of KMnO\(_4\) and \( K_L \) is the constant of Langmuir, \( K_F \) is the constant of Freundlich, and \( K_T \) is the constant Temkin. \( q_{\text{max}} \) (mg g\(^{-1}\)) is the maximum capacity of adsorption. \( B_1 \) and \( n \) are constants of the adsorption heat and the intensity of adsorption, respectively.

**Contact time impact and Kinetic studies.** The experimental data obtained from the adsorption Batch experiments, adsorption of KMnO\(_4\) by Ox-FVES with a concentration of 50, 100, and 200 mg L\(^{-1}\) at several times from 0 to 320 min and 27 °C and 190 rpm have been analyzed by three of different kinetic models. Equations (8–10), Pseudo 1st order, Pseudo 2nd order, and Intraparticle diffusion, correspondingly. Then, the achieved results have been used to study each of the conducted time impact, rate, and mechanism of KMnO\(_4\) adsorption by Ox-FVES adsorbent.

\[
\log(Q_e - Q_t) = \log Q_e - K_1 \frac{t}{2.303}
\]  

(8)

\[
\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e}
\]  

(9)

\[
Q_t = K_{\text{dif}} \sqrt{t} + C
\]  

(10)

\( Q_e \) (mg g\(^{-1}\)): the amount of adsorbed KMnO\(_4\) at time \( t \), \( Q_t \) the amount of adsorbed KMnO\(_4\) at equilibrium, \( K_1 \) (min\(^{-1}\)): rate constants of Pseudo 1st order, \( K_2 \) (g mg\(^{-1}\) min\(^{-1}\)): rate constants of the 2nd order. \( K_{\text{dif}}\) (mg g\(^{-1}\) min\(^{-1}\))\(^{1/2}\) and \( C \) are rate constants of intraparticle diffusion.

**Thermodynamic experiment.** Constants of thermodynamic \( \Delta G^\circ, \Delta H^\circ, \) and \( \Delta S^\circ \) have been also evaluated from the outcomes of experimental Conditions impact part for adsorption of 500, 700, 1000, and 1200 mg L\(^{-1}\) KMnO\(_4\) solutions according to Eqs. (11) and (12).
where $\Delta S^\circ$, $\Delta G^\circ$, and $\Delta H^\circ$ are the change in standard entropy, change in standard free energy, and is the change in standard enthalpy, $T$ and $R$ are the adsorption temperature of (K) and universal gases constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), respectively.

Results and discussion

**FVESPs characterization.** The FT-IR spectra of four samples of modified and unmodified FVESPs are revealed in Fig. 1. It can be observed from the figure that the unmodified FVESPs sample has six peaks at 1060 cm$^{-1}$ for C–O stretching, 1118 cm$^{-1}$ for C–O stretching of a secondary alcohol, 1025 cm$^{-1}$ for C–F stretch Aliphatic fluoro compounds, 1590 cm$^{-1}$ for C=C stretching, 2870 cm$^{-1}$ and 2940 cm$^{-1}$ for stretching the C–H alkane, and 3360 cm$^{-1}$ for hydrogen bond stretching of the O–H. Figure 1 illustrates also that the modified Zn-FVESPs and Zn/Cu-FVESPs adsorbents showed the same peaks with a slight shift, while in the case of Ox-FVESPs sample, many peaks developed (Fig. 1), and these bands are 1190 cm$^{-1}$, 1320 cm$^{-1}$, and 1620 cm$^{-1}$. The appearance of these bands support the success of the chemical modification process that was carried out for the adsorbent and also confirms the variety of functional groups on the surface of Ox-FVESPs, which will have an effective role in permanganate adsorption from the water later.

The spectrum of FVESPs, Zn-FVESPs, Ox-FVESPs, and Zn/Cu-FVESPs SEM images are demonstrated in Fig. 2a–d, respectively. When comparing the SEM images of modified samples (b), (c), and (d) to the unmodified adsorbent (a), it can be seen that the surface of the FVESPs adsorbent has been significantly transformed by modification procedure, as most of the modified adsorbents pleats have been distorted and their structures became scattered. Furthermore, several heterogeneous holes and pores have appeared on the modified adsorbents surfaces, which improve the adsorption performance. It is also recognized from Fig. 2c that the density of micropores of the modified adsorbent is more than the rest of the other samples.

The relationship between pH$_i$ and pH$_i$–pH$_f$ is depicted in Fig. 3, which shows that pH$_{ZPC}$ (the solution pH when the surface of sorbent has a zero net charge) is 7.2. Meanwhile, the surface charge of the adsorbent will be positive and negative at solution pH levels lower and higher than 7.2, Al-Aoh$_{25}^{25}$ has previously found similar findings.

BET surface analyzer results for the modified and unmodified FVESPs samples are listed in Table 1, Surface Area (m$^2$ g$^{-1}$), Volume of Pore (cm$^3$ g$^{-1}$), and Size of Pore (Å). The table shows that the Ox-FVESPs sample achieved the highest surface area (0.6806 m$^2$ g$^{-1}$) and size of the pore (522.063 Å) compared to the rest of the other samples. The highest values of the surface area and size of pore will positively affect the process of permanganate adsorption on the modified FVESPs surface by oxalic acid and prove that the modification process has an important and obvious role.

**The idealistic adsorbent identification.** Figure 4 illustrates the percentage removal for KMnO$_4$ adsorption by four different samples that were synthesized and modified in this work, and it was as the following 80.52 for FVESPs, 64.03 for Zn-FVESPs, 89.36 for Ox-FVESPs, and 49.08 for Zn/Cu-FVESPs. The percentage removal
Figure 2. SEM images of (a) FVESP and (b) Zn-FVESP and (c) Ox-FVESP and (d) Zn/Cu-FVESP.
values show that the Ox-FVES adsorbent has the greatest percentage among other samples, so, these findings support the Ox-FVES adsorbent is the best sample for KMnO₄ adsorption. Also, these results were fully consistent with the SEM and BET surface outcomes. As a result, only Ox-FVES adsorbent was used in the rest of this study.

Experimental conditions impact. Influence of pH solution. The adsorption performance is greatly influenced by the pH of the adsorbate solution, degree of ionization, and charge of adsorbent of the dye molecules also impacted by pH. As a result, the impact of this issue was addressed in this study (Fig. 5). It is clear from the figure that the $q_e$ (mg g⁻¹) value was greatly affected by the pH values, as it was high when pH values were raised from 1.5 to 7.2, and this is due to the high attraction between the positive charges of the Ox-FVES surface and

![Figure 3. pH_{ZPC} of the Ox-FVES adsorbent.](image)

![Figure 4. The percentage removal for KMnO₄ adsorption by four different samples.](image)

![Figure 5. The pH solution impact on the of KMnO₄ adsorption by Ox-FVES adsorbent.](image)

| Sample       | Surface area (m² g⁻¹) | Volume of pore (cm³ g⁻¹) | Size of pore (Å) |
|--------------|-----------------------|--------------------------|-----------------|
| FVES         | 0.0249                | 0.00153                  | 53.001          |
| Ox-FVES      | 0.6806                | 0.00215                  | 522.063         |
| Zn-FVES      | 0.3087                | 0.00214                  | 91.717          |
| Zn/Cu-FVES   | 0.3979                | 0.00061                  | 91.037          |

Table 1. BET surface analyzer of FVES, Ox-FVES, Zn-FVES, and Zn/Cu-FVES.
the MnO$_4^-$ anions. In contrast, increasing the pH value over 7.2 has a negative effect on $q_e$ (mg g$^{-1}$) because of the significant repulsion between the negative MnO$_4^-$ ions and the negative charges of this adsorbent surface. Like results have been found for the KMnO$_4$ elimination by chemically modified sage leaves powder$^{24}$.

**Impact of Ox-FVES doses.** To specify the ideal mass of Ox-FVES that will be required for the KMnO$_4$ adsorption the percent removal of KMnO$_4$ was plotted against Ox-FVES doses (Fig. 6). The values of percent removal of KMnO$_4$, % R are improved by increasing the mass of Ox-FVES from 0.005 to 0.020 g. This rise was caused by the improvement of the active sites on the Ox-FVES surface, which is related to the adsorbent quantity$^{34}$. Figure 6 shows also the percent R value does not change significantly when the mass of the adsorbent is increased from 0.020 to 0.035 g and it is assumed that the amount of dye adsorption was significantly affected by the concentration of unfilled dynamic reactive sites due to the bonding ability of the adsorption surface function$^{35,36}$. In this study, 0.020 g of Ox-FVES was chosen as the optimal dose. The adsorption of CR dye by Zn/Cu-TPLL adsorbent$^{23}$ and KMnO$_4$ on the CuS surface showed a similar Patten$^{37}$.

**Temperature impact and isotherm studies.** The impact of initial solution concentration and temperature on the adsorption capacity of this work is demonstrated in Fig. 7. Figure 7 shows the relationship between the adsorption amount $Q_e$ (mg/g) and the concentration of KMnO$_4$ (10–1400 mg L$^{-1}$) at 27, 42, and 57 °C temperatures. It can be observed from the figure that raising the temperature of the solution has a positive impact on the adsorption capacity of KMnO$_4$ by Ox-FVES. And this refers to the decreasing of KMnO$_4$ viscosity with solution temperature increasing, also, the kinetic energy of the permanganate particles increases with rising the temperature; the same kinetic energy performance for permanganate ions was recorded by neem leaves powder adsorbent$^{25}$. It is also noted from the same figure that the adsorption of permanganate is improved by raising the concentration of KMnO$_4$ from 10 to 1400 (mg L$^{-1}$) at the same temperature. And this could be supported by the finding that raising the adsorbate concentration will develop the dynamic force$^{38}$, which lowers the resistance of KMnO$_4$ particles mass movement between the Ox-FVESF surface and adsorbate solution. It is also clear that the adsorbent will be effective even at KMnO$_4$ concentrations higher than 1400 mg L$^{-1}$, and this is refer to the unfilled adsorption sites on the adsorbent surface.

Moreover, the outcomes obtained from Batch experiments were analyzed according to the isotherm model of Langmuir (Ce against Ce/qe), isotherm model of Freundlich (ln Ce against ln qe), and isotherm model of Temkin (ln Ce against qe) Fig. 8a–c, the slopes and intercepts of these plots were used to achieve the isotherm parameters and presented in Table 2. Where the experimental results are well fitted by applying the Langmuir isotherm model and the R$^2$ values were the highest compared with Freundlich and Temkin models Table 2, which approves that the Langmuir model is the best fit for this adsorption. These findings also show that the adsorption of KMnO$_4$ is monolayer adsorption and that the Ox-FVES adsorption sites are homogeneous. Same outputs for
KMnO₄ adsorption as recorded by a chemical modified powder from leaves of neem²⁵. Moreover, the Favorable adsorption was confirmed by values of RL which ranged between 0 and 114. Furthermore, high adsorption capacities of 1111.11, 1250.00, and 1428.57 mg g⁻¹ (Table 2) were achieved, at three temperatures that were used in this study. This demonstrates that Ox-FVES₃, as a low-cost and very effective adsorbent, will be of particular importance in the purification of wastewaters from the KMnO₄.

Contact time impact and Kinetic studies. To investigate the contact time impact on the KMnO₄ adsorption experiment, the contact time (t) has been graphed against Qₜ (mg g⁻¹) (adsorption quantity at such time t) for the adsorption of (50, 100, and 200 mg L⁻¹) KMnO₄ concentrations by the ideal dose of chemically modified FVES₃ adsorbent selected for this work (Fig. 9). Figure 9 shows that there are three adsorption regions, the higher adsorption was detected at region I (0–16 min) where the adsorption amount (Qₜ) rapidly augmented, while the increase in region II (16–64 min) was regularly and after 64 min till the end of the experiment time, it was practically consistent (region III). Initially, the removal rate was high due to the availability of the abundant of functional groups³⁹. Similarly, the sharp increase in the rate of removal at the beginning of the adsorption process showed the strong attraction forces between OX-FVES₃ sites and KMnO₄. The same results for KMnO₄

| Temperature | Isotherm parameters |
|-------------|---------------------|
|             | Langmuir            | Freundlich          | Temkin |
|             | q_max (mg g⁻¹) | K_L (L mg⁻¹) | R² | K_f (mg g⁻¹) (L mg⁻¹) | 1/n | n | R² | K_T (L mg⁻¹) | B₁ | R² |
| 27 °C       | 1111.11            | 0.00392           | 0.15408 | 0.996 | 6.2557 | 0.792 | 1.2625 | 0.988 | 0.18027 | 142.58 | 0.871 |
| 42 °C       | 1250.00            | 0.00561           | 0.11294 | 0.994 | 9.5735 | 0.796 | 1.2560 | 0.982 | 0.25209 | 163.59 | 0.878 |
| 57 °C       | 1428.57            | 0.00928           | 0.07144 | 0.994 | 13.6154 | 0.785 | 1.2740 | 0.975 | 0.42520 | 182.81 | 0.886 |

Figure 8. (a) Langmuir and (b) Freundlich and (c) Temkin isotherm models for adsorption of KMnO₄ by Ox-FVES₃.

Table 2. Isotherm constants of Langmuir and Freundlich and Temkin models for KMnO₄ adsorption by Ox-FVES₃.
adsorption were obtained by a powder of sage leaves modified by zinc chloride\textsuperscript{24} and for the adsorption of Cu(II) ions on the nanomaterials surface absorbent\textsuperscript{40}. It is also noted from the same figure that the equilibrium time occurred at the 45th minute of the experiment time.

Furthermore, the experimental outcomes of this adsorption have been studied according to Pseudo-first order, pseudo-second order, and Intraparticle diffusion kinetics models Figs. 10a,b, and 11. The slopes and intercepts of these plots were used to calculate the kinetic parameters and summarized in Tables 3 and 4, the linear relationships observed by applying the pseudo-second order model in Fig. 10b, where the highest R\textsuperscript{2} values occurred.

Figure 9. Impact of adsorption time on KMnO\textsubscript{4} adsorption by Ox-FVESPM.

Figure 10. (a) Kinetic model of the 1st order and (b) Kinetic model of the 2nd order for KMnO\textsubscript{4} adsorption by Ox-FVESPM.

Figure 11. Model of intra-particle diffusion for KMnO\textsubscript{4} adsorption by Ox-FVESPM.
and the good agreement between the experimental $Q_e$ values (Table 3) and computed values of $Q_e$, which approve that the adsorption of this work followed the second-order kinetic model. And implying that the biosorption of KMnO₄ from the aqueous media is governed by a chemical kinetic mechanism involving electron exchange or sharing between the anionic part of the dye ($\text{MnO}_4^{-}$) and the functional groups on the OX-FVESp adsorbent surface. Similar findings were stated for KMnO₄ adsorption by activated carbon⁰¹, nanoparticles prepared from copper sulfide⁰², and powder sage leaves modified by zinc chloride⁰³. The dye adsorption process by modified activated carbon adsorbents followed also the pseudo-second order⁰⁴,⁰⁵.

Intra-particle diffusion plots for KMnO₄ adsorption by Ox-FVESp (Fig. 10) and $R^2$ values, Table 4 display that the relationship between contact time ($t$) and adsorption amount ($Q_t$) could not be linear at all, but two different areas are observed. Furthermore, all the plots do not cross the original and this approves that the adsorption of MnO₄$^{-}$ ions is not affected by the Intra-particle diffusion step; migration of MnO₄$^{-}$ ions via the Ox-FVESp pores will be very simple. This agrees with the SEM results, as it was clear that the Ox-FVESp surface has a lot of asymmetrical pores.

### Thermodynamic experiment

Equation (11) was applied to evaluate parameters of the thermodynamic $\Delta H^\circ$, $\Delta S^\circ$ at three different temperatures for solution Initial concentrations 500, 700, 1000, and 1200 mg L⁻¹. Then, the values of $\Delta G^\circ$ were computed according to Eq. (12) based on the previously calculated values of $\Delta S^\circ$ and $\Delta H^\circ$ and illustrated in Table 5. The lowering in the randomness and the endothermic process of permanganate adsorption by Ox-FVESp adsorbent was confirmed by the positive values of each $\Delta S^\circ$ and $\Delta H^\circ$ (Table 5). Moreover, the $\Delta H^\circ$ values are higher than 20.9 kJ mol⁻¹, ranging from 27.541 to 34.371 kJ mol⁻¹, which indicates the molecules of adsorbate were chemically adsorbed at the adsorbent surface sites, these results are in agreement with the previous kinetic outputs. Negative values of $\Delta G^\circ$ suggest spontaneous adsorption in the range of temperature that is used in this study, similar findings were stated for KMnO₄ adsorption by modified Powder of Ocimum basilicum⁰⁶ and other adsorbents developed from very low-cost adsorbents⁰³,⁰⁴, the adsorption process by cationic polymeric adsorbent also achieved similar results⁰⁷.

### Comparative study with other adsorbents

Table 6 summarized the adsorption capacities of KMnO₄ removal by Ox-FVESp at three temperatures and the capacities of other synthesized low-cost adsorbents. As presented in Table 6, Ox-FVESp adsorbent has a higher adsorption capacity than the conventional low-cost adsorbents that were previously employed to remove MnO₄ from aqueous samples. As a result, the cost-effectiveness of Ox-FVESp, easy availability, and its high performance in adsorption of permanganate from polluted water give this adsorbent a strong opportunity over other adsorbents.

| Table 3. Parameters of the 1st and 2nd-order kinetic models for adsorption of KMnO₄ by Ox-FVESp. |
|---|---|---|---|---|---|
| $C_0$ (mg L⁻¹) | $Q_{exp}$ (mg g⁻¹) | Kinetic model | 1st order | 2nd order |
| | | | $Q_{cal}$ (mg g⁻¹) | $K_1$ (h⁻¹) | $R^2$ | $Q_{cal}$ (mg g⁻¹) | $K_2$ (g mg⁻¹ h⁻¹) | $R^2$ | Rate |
|---|---|---|---|---|---|---|---|
| 50 | 40.89 | 13.14 | 0.0212 | 0.85 | 41.67 | 0.0046 | 0.999 | 0.19308 |
| 100 | 79.87 | 43.14 | 0.0180 | 0.898 | 83.33 | 0.0009 | 0.999 | 0.07481 |
| 200 | 154.57 | 93.86 | 0.0246 | 0.958 | 161.29 | 0.0005 | 0.999 | 0.08832 |

| Table 4. Parameters of the intra-particle-diffusion kinetic model for KMnO₄ adsorption by Ox-FVESp. |
|---|---|---|---|---|
| $C_0$ (mg L⁻¹) | First region | Second region |
| | $K_{dif}$ (mg h⁻¹/² g⁻¹) | $C$ | $R^2$ | $K_{dif}$ (mg h⁻¹/² g⁻¹) | $C$ | $R^2$ |
|---|---|---|---|---|---|---|
| 50 | 5.187 | 5.839 | 0.889 | 0.0743 | 39.59 | 0.973 |
| 100 | 10.990 | 9.413 | 0.993 | 0.4868 | 71.27 | 0.945 |
| 200 | 17.271 | −4.389 | 0.982 | 0.7332 | 142.44 | 0.900 |

| Table 5. Thermodynamic constants for KMnO₄ adsorption by Ox-FVESp. |
|---|---|---|---|---|---|---|
| Initial concentration (mg L⁻¹) | $\Delta H^\circ$ (kJ mol⁻¹) | $\Delta S^\circ$ (kJ mol⁻¹) | $\Delta G^\circ$ (KJ mol⁻¹) | $R^2$ |
| | 300 K | 315 K | 330 K |
| 500 | 34.371 | 0.1227 | −2.4260 | −4.2659 | −6.1057 | 0.997 |
| 700 | 31.346 | 0.1117 | −2.1758 | −3.8519 | −5.5280 | 0.999 |
| 1000 | 29.246 | 0.1024 | −1.4849 | −3.0214 | −4.5580 | 0.992 |
| 1200 | 27.541 | 0.0956 | −1.1374 | −2.5713 | −4.0051 | 0.992 |
Modification of the *F. vulgare* Seeds (FVES) powder was done by each of ZnCl₂, oxalic acid, and CuS, all samples have been characterized by different techniques and examined for permanganate (KMnO₄) adsorption. Among the four modified and unmodified samples, the sample modified by oxalic acid (Ox-FVES) has the highest percentage removal for KMnO₄ adsorption (%R = 89.36), and was nominated as a new adsorbent for KMnO₄ adsorption from the synthesized solutions. The surface area, volume, and size of the pore of the Ox-FVES adsorbent were determined as 0.6806 m² g⁻¹, 0.00215 cm³ g⁻¹, and 522.063 Å, respectively, as pHₚₑₚ also was stated to be 7.2. The influence of KMnO₄ concentration, Ox-FVES dose, pH of the solution, adsorption temperature, and adsorption time on the KMnO₄ adsorption was inspected, it can be noted from the experimental outcomes the adsorption performance of KMnO₄ was positively affected by the rising concentration of KMnO₄ from 10 to 1400 mg L⁻¹. Ox-FVES dose from 0.005 to 0.020 g, contact temperature from 27 to 57 °C, and adsorption time from 0 to 64 min. While the increase of solution pH from 1.5 to 11.5 has a negative effect on the adsorption process. The calculated R² values of different isotherm and kinetic models (0.999 and 0.996) revealed the adsorption performance of KMnO₄ following the Langmuir and Pseudo 2nd order models. Constants of thermodynamic ΔG°, ΔH°, and ΔS° values indicate chemical and spontaneous adsorption at the adsorbent surface. Additionally, high adsorption capacities were accomplished at three temperatures that were used in this work 1111.11, 1250.00, and 1428.57 mg g⁻¹. Proposing that the Ox-FVES adsorbent prepared from very low-cost material was important to explore the use in the water purification from dye at optimum conditions.

### Data availability
The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request. And I state that the experimental research on plant seeds used in this study complied with the relevant institutional, national, and international guidelines and legislation.

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### Table 6. Adsorption capacities for KMnO₄ removal by several adsorbents.

| Adsorbant                        | Temperature (°C) | Q (mg g⁻¹) | Reference                        |
|---------------------------------|-----------------|------------|----------------------------------|
| Ox-FVES                         | 27              | 1111.11    | This study                       |
|                                 | 42              | 1250.00    |                                  |
|                                 | 57              | 1428.57    |                                  |
| Granular activated charcoal     |                 | 57.47      | [1]                              |
| Animal bone-derived activated carbon |             | 28.04      | [14]                             |
| Corncob derived activated carbon |                 | 26.00      | [14]                             |
| Coconut shells-derived activated carbon |          | 23.25      | [12]                             |
| Modified activated carbonaceous materials |       | 100.00     | [10]                             |
| Zinc chloride Ocimum basilicum leaves powder | | 25         | 588.235 | [10] |
|                                 | 35              | 625.000    |                                  |
|                                 | 45              | 666.667    |                                  |
|                                 | 55              | 714.286    |                                  |

**Conclusions**

Modification of the *F. vulgare* Seeds (FVES) powder was done by each of ZnCl₂, oxalic acid, and CuS, all samples have been characterized by different techniques and examined for permanganate (KMnO₄) adsorption. Among the four modified and unmodified samples, the sample modified by oxalic acid (Ox-FVES) has the highest percentage removal for KMnO₄ adsorption (%R = 89.36), and was nominated as a new adsorbent for KMnO₄ adsorption from the synthesized solutions. The surface area, volume, and size of the pore of the Ox-FVES adsorbent were determined as 0.6806 m² g⁻¹, 0.00215 cm³ g⁻¹, and 522.063 Å, respectively, as pHₚₑₚ also was stated to be 7.2. The influence of KMnO₄ concentration, Ox-FVES dose, pH of the solution, adsorption temperature, and adsorption time on the KMnO₄ adsorption was inspected, it can be noted from the experimental outcomes the adsorption performance of KMnO₄ was positively affected by the rising concentration of KMnO₄ from 10 to 1400 mg L⁻¹, Ox-FVES dose from 0.005 to 0.020 g, contact temperature from 27 to 57 °C, and adsorption time from 0 to 64 min. While the increase of solution pH from 1.5 to 11.5 has a negative effect on the adsorption process. The calculated R² values of different isotherm and kinetic models (0.999 and 0.996) revealed the adsorption performance of KMnO₄ following the Langmuir and Pseudo 2nd order models. Constants of thermodynamic ΔG°, ΔH°, and ΔS° values indicate chemical and spontaneous adsorption at the adsorbent surface. Additionally, high adsorption capacities were accomplished at three temperatures that were used in this work 1111.11, 1250.00, and 1428.57 mg g⁻¹. Proposing that the Ox-FVES adsorbent prepared from very low-cost material was important to explore the use in the water purification from dye at optimum conditions.

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|                                 | 45              | 666.667    |                                  |
|                                 | 55              | 714.286    |                                  |
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Author contributions

Methodology, validation, conceptualization formal analysis, investigation, writing—original draft, writing—reviewing & editing.

Competing interests

The author declares no competing interests.
