Potassium Permanganate Dye Removal from Synthetic Wastewater Using A Novel, Low-Cost Adsorbent, Modified from The Powder of Foeniculum Vulgare Seeds

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

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Abstract

Seeds powder of *Foeniculum vulgare* (FVE) was used to prepare a novel adsorbent, the new adsorbent was characterized and its ability to eliminate potassium permanganate (KMnO_4) was examined. The impact of KMnO_4 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 *Foeniculum vulgare* seeds powder (FVESP) adsorbent were determined as $0.6806 \text{ m}^2 \text{ g}^{-1}$, $0.00215 \text{ cm}^3 \text{ g}^{-1}$, and $522.063 \text{ \AA}$, as pH_{ZPC} of oxalic acid FVESP (Ox- FVESP) was stated to be 7.2. The R^2 values obtained from applying different isotherm and kinetic models (0.999 and 0.996) showed that the adsorption performance of KMnO_4 follows the Langmuir and Pseudo 2nd order models. Furthermore, high adsorption capacities of 1111.11, 1250.00, and 1428.57 (mg/g) 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.

Keywords: Low-cost adsorbent, Modification, Synthetic Wastewater, Potassium permanganate Removal.

1. Introduction

Potassium permanganate (KMnO_4) is a highly strong oxidizing agent that is commonly used for water purification from numerous pollutants, mainly for the destruction of compounds that causing undesirable taste, odor, and color for the treated water [1]. Remarkably, permanganate is still one of the most oxidizing chemicals ever applied to remove each iron, manganese, and arsenic from water [2, 3], In addition to its great ability to oxidize cyanide, phenols, and organic compounds [4-8].

Recently, many studies reported that the excessive exposure to permanganate may cause acute problems of the nervous system, irritation of the skin and eye, Furthermore, it was stated that the manganese has significant toxicity towards the liver and kidneys [9, 10]. Therefore many techniques and methods have been applied for KMnO_4 removal from the contaminated water. For instance, fluidized-bed crystallization method was used [11], 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 [1], activated carbon is a common adsorbent that used for adsorption of KMnO_4 from polluted water due to its high adsorption efficiency [12].

To remove potassium permanganate molecules from polluted aqueous solutions by adsorption a lot of activated carbon adsorbents were prepared using shells of coconut [12], corn cob, and animal bone were also applied [13], sulfuric acid modification of activated carbon, and activated charcoal have been used too [1, 14]. More recently, Nanoparticles of metallic oxides have been used to remediate effluent from various dyes [15–21], Copper sulfide nanoparticles were used as dynamic adsorbents to treat the synthetic wastewater from potassium permanganate ions [22].

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 [23] Neem [24], *Nitraria retusa* [25], and *Ocimum basilicum* [26] were used as low-cost sorbents to remove Permanganate anions from synthetic samples.

Foeniculum vulgare plant (FVE) is well-known by fennel in many countries and as shamr in Saudi Arabia, mainly used as food and tea flavored and considered as a flavored spice, its seeds were used as antitumor [27], antimicrobial [28], and antioxidant [29]. Gold nanoparticles based on seeds extract of fennel FVE was synthesized and its catalytic activity against rhodamine B and methylene blue dyes were examined [30], V_2O_5 - Fe_2O_3 nanocomposites from stem powder of FVE have been produced and the catalytic performance of nanocomposites particles was assessed for reduction of 4-nitrophenol [31].

Up to now, no adsorbent based on FVE seeds (FVES) was prepared in any form and applied to eliminate the hazardous dyes from water even permanganate ions, despite the excellent medical properties of FVE herb, in addition to its widespread over the world. Therefore, this research mainly aimed to prepare a new adsorbent from seeds of FVE and to investigate the adsorbent performance toward eliminating $KMnO_4$ 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 $KMnO_4$ removal experiment, as the adsorption capacity of modified adsorbent for removal of $KMnO_4$ will be critically addressed.

To achieve all the desired goals of this work and get the best results, unmodified samples from FVES have been synthesized and the modification has been also carried by zinc chloride, copper

sulfide, and oxalic acid; both types of samples have been characterized and examined as adsorbents for KMnO_4 removal from water, to choose the best adsorbent, the adsorption performances have been compared, then all the KMnO_4 adsorption experimental factors and conditions of selected adsorbent were tested.

2. Materials and Methodology

2.1 Materials

Seeds of FVE were obtained from a local market in Tabuk City, KSA. All chemicals that were used in this work were obtained from Sigma-Aldrich with purity of (37%) for hydrochloric acid, $\geq 97\%$ for sodium hydroxide $\geq 97\%$ for zinc chloride, $\geq 99.99\%$ for oxalic acid, $\geq 99.99\%$ for copper sulfide, and $\geq 99.00\%$ for sodium carbonate.

2.2. Methodology

2.2.1. Preparation and Modification of FVESP

The FVE seeds were washed with distilled water several times and then dried overnight, after that the powder from the FVE seeds (FVESP) was obtained by an electric grinder. A sample of 100 g was refluxed 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 grinded and sieved, and the resulted adsorbent 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 were labeled also Zn-FVESP, and Zn/Cu- FVESP.

2.2.2. 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 carried out. The surface area and porosity of each adsorbent were estimated using BET (NOVA-2200 Ver. 6.11) technology for 22 hours and 77.35 K. In addition, 40 mL of 0.05 M Na_2CO_3 solutions varying with 2, 4, 6, 8, and 10 initial values of pH_i have been mixed in a 150 mL plastic container with 0.2 g of the idealistic adsorbent. After shaking all containers for 26 hours 175 rpm and 27° C conditions in a shaker incubator, filtration of each was done, then using a pH meter, the final pH (pH_f) of each solution was determined. Finally, to determine the pH_{ZPC} value of this adsorbent, the values of ($\text{pH}_i - \text{pH}_f$) have been calculated and graphed against the pH_i values.

2.2.3. Experiments on Adsorption

2.2.3.1. The Idealistic Adsorbent Identification

To determine the superlative as well as the most efficient adsorbent developed in the current study for KMnO_4 removal from synthetic aqueous samples, 20 mL of 100 mg/L KMnO_4 solution concentration was combined with 0.03g of FVESP in a 30 mL amber bottle. A shaker incubator was used for 30 hours to stirrer the sealed amber bottle at 27° C and 180 rpm. After that, the

114 mixture was filtered; The Jenway UV-6800 UV-Vis spectrophotometer was used at 525 nm to
 115 measure the balanced concentration of KMnO₄ in the filtrate. The same procedure was repeated
 116 with Ox- FVESP, Zn- FVESP, and Zn/Cu- FVESP adsorbents for the KMnO₄ adsorption.
 117 Equations (I) and (II) were used to calculate the KMnO₄ percentage removal percent %R and the
 118 quantities of KMnO₄ adsorbed at equilibrium Q_e (mg g⁻¹) by both modified and unmodified
 119 adsorbents.

$$\%R = \frac{C_o - C_e}{C_o} 100\% \quad \dots\dots\dots (I)$$

$$Q_e = \frac{V}{m} (C_o - C_e) \quad \dots\dots\dots (II)$$

120 Where C_o is the KMnO₄ initial concentration and C_e is the KMnO₄ final concentration, m, and V
 121 are the mass of adsorbent (g), and KMnO₄ solution volume (L), respectively.

122 **2.2.3.2. Experimental Conditions impact**

123 Batch experiments have been conducted to observe and identify the most significant factors that
 124 affect KMnO₄ adsorption experiments by ideal adsorbent Ox- FVESP, such as concentration of
 125 KMnO₄ (10-1400 mg L⁻¹), contact time (0-320 min), the dosage of Ox- FVESP adsorbent
 126 (0.005- 0.035 g), the adsorption temperature (27- 57°C), and the pH (1.5-11.5). All of the Batch
 127 experiments have been done in 30 ml amber bottles by adding 20 mL of KMnO₄ solution to
 128 enough amounts from Ox- FVESP. A shaker incubator at 180 rpm was used to shake all sealed
 129 amber bottles for a required time, followed by filtration of each mixture, and the remaining
 130 concentrations of KMnO₄ were measured as mentioned previously in part 4.2.1

131 To compute the adsorbed amount of KMnO₄ at equilibrium (Q_e, mg g⁻¹) by the Ox- FVESP
 132 adsorbent and time t (Q_t, mg g⁻¹) equations (II) and (III) were applied.

$$Q_t = \frac{V}{m}(C_o - C_t) \dots\dots\dots (III)$$

133 Where C_t (mg.L⁻¹) is the KMnO₄ concentration of at contact time.

134 2.2.3.3. Temperature impact and isotherm studies

135 The outcomes obtained from Section 2.2.3.2 for 10-1400 mg/L KMnO₄ solutions by 0.02 g by
 136 Ox- FVESP adsorbent at 26 h contact time and three different temperatures (27, 42, and 57° C)
 137 and 190 rpm have been analyzed according to the three isotherm models, Langmuir, Freundlich,
 138 and Temkin linear forms, equations (IV, V, VI) respectively. The parameter of equilibrium R_L
 139 value of the Langmuir isotherm model was also evaluated according to Equation (VII).

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \dots\dots\dots (IV)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \dots\dots\dots (V)$$

$$q_e = B_1 \ln K_T + B_1 \ln C_e \dots\dots\dots (VI)$$

$$R_L = \frac{1}{1 + K_L C_o} \dots\dots\dots (VII)$$

140 Where C_o is the maximum initial concentration of KMnO₄ and K_L is the constant of Langmuir,
 141 K_F is the constant of Freundlich, and K_T is the constant Temkin. q_{max} (mg/g) is the maximum

capacity of adsorption. B1 and n are constants of the adsorption heat and the intensity of adsorption, respectively.

2.2.3.4. Contact time impact and Kinetic studies

The experimental data obtained from the adsorption Section 2.2.3.2, adsorption of KMnO₄ by Ox- FVESP 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 (VIII), (IX), and (X), Pseudo 1st order, Pseudo 2nd order, and Intraparticle diffusion, correspondingly. Then, the achieved results have been used to the study each of the conducted time impact, rate, and mechanism of KMnO₄ adsorption by Ox- FVESP adsorbent.

$$\log(Q_e - Q_t) = \log Q_e - K_1 \frac{t}{2.303} \quad \text{..... (VIII)}$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad \text{..... (IX)}$$

$$Q_t = K_{dif} \sqrt{t} + C \quad \text{..... (X)}$$

Q_t (mg g⁻¹): the amount of adsorbed KMnO₄ at time t, Q_e: the amount of adsorbed KMnO₄ at equilibrium, K₁ (1/min): rate constants of Pseudo 1st order, K₂: (g mg⁻¹ min⁻¹) rate constants of the 2nd order. K_{dif} (mg g⁻¹ min⁻¹)^{1/2} and C are rate constants of intraparticle diffusion.

2.2.3.5. Thermodynamic experiment

Constants of thermodynamic ΔG°, ΔH°, and ΔS° have been also evaluated from the outcomes of Section 2.2.3.2 for adsorption of 500, 700, 1000, and 1200 mg L⁻¹ KMnO₄ solutions according to equations (XI) and (XII).

$$\ln\left(\frac{Q_e}{C_e}\right) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad \text{..... (XI)}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{..... (XII)}$$

Where ΔS° , ΔG° , and ΔH° 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 J/K mol), respectively.

3. Results and Discussion

3.1. FVESP Characterization

The FT-IR spectra of four samples of modified and unmodified FVESP are revealed in Figures 1. It can be observed from the figure that the unmodified FVESP 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- FVESP, and Zn/Cu- FVESP adsorbents showed the same peaks with a slight shift, while in the case of Ox- FVESP sample, many peaks developed (Figure 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- FVESP, which will have an effective role in permanganate adsorption from the water later.

The spectrum of FVESP, Zn- FVESP, Ox- FVESP, and Zn/Cu- FVESP SEM images are demonstrated in Figures 2(a), 2(b), 2(c), and 2(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 FVESP 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 Figure 2(c) 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 Figure 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] has previously found similar findings.

BET surface analyzer results for the modified and unmodified FVESP samples are listed in table 1, Surface Area ($m^2 g^{-1}$), Volume of Pore ($cm^3 g^{-1}$), and Size of Pore ($\text{\AA}$). The table shows that the Ox- FVESP sample achieved the highest surface area ($0.6806 m^2 g^{-1}$) and size of the pore ($522.063 \text{\AA}$) 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 FVESP surface by oxalic acid and prove that the modification process has an important and obvious role.

3.2. 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 FVESP, 64.03 for Zn- FVESP, 89.36 for Ox- FVESP, and 49.08 for Zn/Cu- FVESP. the percentage removal values show that the Ox- FVESP adsorbent has the greatest percentage among other samples, so, these findings support the Ox- FVESP adsorbent is the best sample for $KMnO_4$ adsorption. Also,

these results were fully consistent with the SEM and BET surface outcomes. As a result, only Ox- FVESP adsorbent was used in the rest of this study.

3.3. Experimental Conditions impact

3.3.1. 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 (Figure 5). It is clear from the figure that the qe (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- FVESP surface and the MnO_4^- anions. In contrast, increasing the pH value over 7.2 has a negative effect on qe (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 [23].

3.3.2. Impact of Ox- FVESP doses

To specify the ideal mass of Ox- FVESP that will be required for the KMnO_4 adsorption the percent removal of KMnO_4 was plotted against Ox- FVESP doses and to investigate the adsorbent dosage impact (Figure 6). The values of percent removal of KMnO_4 % R are improved by increasing the mass of Ox- FVESP from 0.005 to 0.020 g. This rise was caused by the improvement of the active sites on the Ox- FVESP surface, which is related to the adsorbent quantity [33]. Figure 6 shows also the percent R value does not change significantly that when the mass of the adsorbent is increased from 0.020 g to 0.035 g because the adsorbent particles will be gathered to form a cluster at high doses [34]. In this study, 0.020 g of Ox- FVESP was

chosen as the optimal dose. The adsorption of CR dye by Zn/Cu-TPLLP adsorbent [22] and KMnO_4 on the CuS surface showed a similar Pattern [35].

3.3. Temperature impact and isotherm studies

The impact of initial solution concentration and temperature on the adsorption capacity of this work is demonstrated in figure 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 rising the temperature of the solution has a positive impact on the adsorption capacity of KMnO_4 by Ox- FVESP. 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 [24]. It is also noted from the same figure that the adsorption of permanganate is improved by rising the concentration of KMnO_4 from 10 to 1400 (mg/L) at the same temperature. And this could be supported by the finding that rising the adsorbate concentration will develop the dynamic force, which lowers the resistance of KMnO_4 particles mass movement between the Ox- FVESP surface and adsorbate solution [32]. It is also clear that the adsorbent will be effective even at KMnO_4 concentrations higher than 1400 (mg/L), and this is refer to the unfilled adsorption sites on the adsorbent surface.

Moreover, The outcomes obtained from Section 2.2.3.2 were analyzed according to the isotherm model of Langmuir (C_e against C_e/q_e), isotherm model of Freundlich ($\ln C_e$ against $\ln q_e$), and isotherm model of Temkin ($\ln C_e$ against q_e) Figure 8 (a, b, and 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- FVESP adsorption sites are homogeneous. Same outputs for KMnO_4 adsorption as recorded by a chemical modified powder from leaves of neem [24]. Moreover, the Favorable adsorption was confirmed by values of R_L which ranged between 0 and 1 [13].

Furthermore, high adsorption capacities of 1111.11, 1250.00, and 1428.57 (mg/g) (Table 2) were achieved, at three temperatures that were used in this study. This demonstrates that Ox- FVESP, as a low-cost and very effective adsorbent, will be of particular importance in the purification of wastewaters from the KMnO_4 .

3.4. Contact time impact and Kinetic studies

To investigate the contact time impact on the KMnO_4 adsorption experiment, the contact time (t) has been graphed against Q_t (mg/g) (adsorption quantity at such time t) for the adsorption of (50, 100, and 200 mg/L) KMnO_4 concentrations by the ideal dose of chemically modified FVESP adsorbent selected for this work (Figure 9). Figure 9 shows that there are three adsorption regions, the region I (0-16 min) where the adsorption amount (Q_t) rapidly augmented, while the increase in region II (16-64 min) was regularly and after 64 minutes till the end of the experiment time, it was practically consistent (region III). This indicates that the majority of the adsorbent sites were empty at the start of the adsorption process, and with time all the OX- FVESP sites became full of KMnO_4 particles. The same results for KMnO_4 adsorption were obtained by a powder of sage leaves modified by zinc chloride [23]. 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 figure 10 (a), (b), and figure 11. The slopes and intercepts of these plots were used to calculate the kinetic parameters and summarized in table (3) and (4), the linear relationships observed by applying the pseudo- second order model in Figure 10 (b), where the highest R^2 values occurred, and the good agreement between the experimental Q_e values (table 4) and computed values of Q_e , which approve that the adsorption of this work followed the second-order kinetic model. And implying that the MnO_4^- ions have chemically interacted with functional groups on the OX- FVESP surface. Similar findings were stated for $KMnO_4$ adsorption by activated carbon [12], nanoparticles prepared from copper sulfide [22], and powder sage leaves modified by zinc chloride [23].

Intra-particle diffusion plots for $KMnO_4$ adsorption by Ox- FVESP figure 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 MnO_4^- ions is not affected by the Intra-particle diffusion step; migration of MnO_4^- 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.

3.5. Thermodynamic experiment

Equation (XI) was applied to evaluate parameters of the thermodynamic ΔH° , and ΔS° at three different temperatures for solution Initial concentrations 500, 700, 1000, and 1200 (mg/L). Then, the values of ΔG° were computed according to equation (XII) based on the previously calculated values of ΔS° and ΔH° and illustrated in Table 5. The lowering in the randomness and the

endothermic process of permanganate adsorption by Ox- FVESP adsorbent were confirmed by the positive values of each ΔS° and ΔH° (table5) [26]. Moreover, the ΔH° values are higher than 20.9 kJ/mol, ranging from 27.541 to 34.371kJ/mol, 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 ΔG° suggest spontaneous adsorption in the range of temperature that is used in this study, similar findings were stated for KMnO_4 adsorption by modified Powder of *Ocimum basilicum* [26] and other adsorbents developed from very low-cost materials [22,23].

3.6. A comparative study with other adsorbents

Table 6 summarized the adsorption capacities of KMnO_4 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 KMnO_4 from aqueous samples. As a result, The low cost of preparing Ox- FVESP and its high performance in adsorption of permanganate from polluted water give this adsorbent a strong opportunity over other adsorbents.

4. Conclusions

Modification of the *Foeniculum vulgare* Seeds (FVES) powder was done by each of ZnCl_2 , oxalic acid, and CuS , all samples have been characterized by different techniques and examined for permanganate (KMnO_4) adsorption. Among the four modified and unmodified samples the sample modified by oxalic acid (Ox- FVESP) has the highest percentage removal for KMnO_4 adsorption (%R = 89.36), and was nominated as a new adsorbent for KMnO_4 adsorption from the synthesized solutions. The surface area, volume, and size of the pore of the Ox- FVESP

adsorbent were determined as $0.6806 \text{ m}^2 \text{ g}^{-1}$, $0.00215 \text{ cm}^3 \text{ g}^{-1}$, and $522.063 \text{ \AA}$, respectively, as pH_{ZPC} also was stated to be 7.2. The influence of KMnO₄ concentration, Ox- FVESP 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, Ox- FVESP dose from 0.005 to 0.020 g, contact temperature from 27-57 °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 R^2 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). This will draw attention to use Ox- FVESP adsorbent prepared from very low-cost material to purify water from permanganate.

Availability of data and materials

All data generated or analyzed during this study are available with the authors.

Competing interests

The authors declare they have no competing interests.

Authors' contributions

Methodology, Validation, Conceptualization Formal analysis, Investigation, Writing – Original Draft, Writing – Reviewing & Editing.

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Figure caption

Figure 1:	Spectra of FT-IR for the FVESP, Ox- FVESP, Zn- FVESP, and Zn/Cu- FVESP.
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488 **Fig. 1**

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Fig. 3

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Fig. 5

Fig. 6

Fig. 7

617 **Fig. 8**

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Fig. 9

Fig. 10

Fig. 11

Table 1

Sample	Surface Area (m ² .g ⁻¹)	Volume of Pore (cm ³ .g ⁻¹)	Size of Pore (Å)
FVESP	0.0249	0.00153	53.001
Ox- FVESP	0.6806	0.00215	522.063
Zn- FVESP	0.3087	0.00214	91.717
Zn/Cu- FVESP	0.3979	0.00061	91.037

Table 2

Temperature	Isotherm parameters										
	Langmuir				Freundlich				Temkin		
	$q_{\max}$ (mg.g ⁻¹)	K_L (L.mg ⁻¹)	R_L	R^2	K_F (mg.g ⁻¹) (L.mg ⁻¹) ^{1/n}	1/n	n	R^2	K_T (L.mg ⁻¹)	B_1	R^2
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

Table 3

C_0 (mg.L ⁻¹)	$Q_{e,exp}$ (mg.g ⁻¹)	Kinetic model						
		1 st order			2 nd order			
		$Q_{e1,cal}$ (mg.g ⁻¹)	K_1 (h ⁻¹)	R^2	$Q_{e2,cal}$ (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	0.998	0.08832

Table 4

C_o (mg.L ⁻¹)	First region			Second region		
	K_{dif} (mg/h ^{1/2} g)	C	R^2	K_{dif} (mg/h ^{1/2} g)	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

Initial concentration (mg.L ⁻¹)	ΔH° (kJ.mol ⁻¹)	ΔS° (kJ.mol ⁻¹)	ΔG° (KJ.mol ⁻¹)			R^2
			300K	315K	330K	
500	34.371	0.1227	-2.4260	-4.2659	-6.1057	0.977
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

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Table 6

Adsorbant	Temprutire	Q(mg/g)	Reference
Ox- FVESP	27 °C	1111.11	This study
	42 °C	1250.00	
	57 °C	1428.57	
Granular Activated Charcoal		57.47	[1]
Animal bone-derived activated carbon		28.04	[13]
Corncob derived activated carbon		26.00	[13]
Coconut shells derived activated carbon		23.25	[12]
Modified activated carbonaceous materials		100,00	[14]
Zinc chloride Ocimum basilicum leaves powder	25 °C	588.235	[35]
	35 °C	625.000	
	45°C	666.667	
	55°C	714.286	