



Removal of paracetamol from water and wastewater by Jordanian olivine: influence of ultrasonication

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ABSTRACT

The removal of the widely used drug (paracetamol) from water using Jordanian olivine was investigated. The olivine was characterized using the scanning electron microscopy-energy dispersive spectroscopy and the Fourier-transform infrared spectroscopy (FT-IR) analyses. The effect of the temperature, contact time, and ultrasonic waves at an ultrasonic frequency of 37 kHz on the removal of paracetamol was considered. The concentration of paracetamol was measured using the FT-IR analysis method. Thermodynamic parameters of adsorption were determined. The kinetics data were obtained under normal conditions and with ultrasonic waves. The percentage of paracetamol removed was increased with increased time in the presence of the ultrasonic waves (with maximum removal of 97.12% at 60 min) using 0.5 g of olivine. The adsorption of paracetamol was found to be unfavorable/non-spontaneous (with ΔG° 2.272–5.075 kJ mol⁻¹), exothermic ($\Delta H^\circ = -2.674$ kJ mol⁻¹) and physisorption in nature. From the kinetics studies, the amount of paracetamol adsorbed (Q_e) was improved due to the combined effects of adsorption with ultrasonic waves. Jordanian olivine can be utilized with great efficiency for the treatment of paracetamol-containing water and wastewater.

Keywords: Paracetamol; Adsorption; Wastewater treatment; Ultrasound; Kinetics.

1. Introduction

The frequent contamination of water resources with pharmaceuticals is one of the most significant environmental

problems. The production of pharmaceutical substances has increased rapidly in the last decades since they are used for the health of humans and animals. A large amount of these pharmaceutical products are discharged into the environment (water and soil) continually through diverse

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sources including human activities, pharmaceutical industries, and hospitals [1]. Pharmaceutical products have been detected in wastewater and surface water as micro-pollutants at ng L^{-1} to $\mu\text{g L}^{-1}$ levels [2]. The first report about the pharmaceutical products in the environment was given by Fielding et al. [3] who discovered some pharmaceuticals and other related compounds in a river and drinking water. In 1983, Watts et al. [4] reported the presence of tetracycline and theophylline in the same river. Enormous attention has been received on the contamination of water with different types of pharmaceutical compounds such as antibiotics, hormones, analgesics, psychotropics, antipyretics, and anti-inflammatories [5,6] due to their environmental impacts and potential adverse effects on human health and aquatic life [7].

Great efforts have been made in the past to improve water treatment processes. Therefore many effective techniques have been developed for the removal of pharmaceutical micro-pollutants from polluted water. Such methods include filtration, advanced oxidation, coagulation, filtration, precipitation, reverse osmosis, ozonation, ion exchange, biodegradation, and adsorption processes [8,9]. It has been demonstrated that most of the conventional wastewater treatment methods are not so effective to eliminate or at least degrading most of the pharmaceutical compounds. Therefore, residual quantities remain in treated water and these have been accumulating in drinking water [10]. At times, the combination of two techniques, for example, the adsorption and advanced oxidation process is more beneficial and effective. Adsorption is one of the most important and widespread processes for water treatment.

Adsorption using porous materials is a very promising technique for the removal of organic and inorganic pollutants [11,12]. Adsorption has a good potential for removing a wide range of contaminants with rapid process kinetics [13]. Another significant benefit of the adsorption process is its simplicity and inexpensive cost of operation/equipment [14,15]. Different types of adsorbent materials have been used for adsorption purposes including activated carbon, charcoal, clay, activated sludge, and graphite [16]. Such adsorbents possess great adsorption capacities for organic and non-organic chemicals in liquid or gaseous phases, so they are usually the first and the best choice of researchers for the purification of water containing harmful chemicals. Activated carbon is the most commonly studied sorbent for the removal of pharmaceuticals from water mainly due to its high surface area and availability in the market [8]. Many promising bio-sorbent materials have also been used for the effective removal of some pharmaceutical products from aqueous environments including black tea residue [17], sugar cane bagasse [18], peach stones [19], olive stones [20], mango peels [21], cork powder [19], and coconut mesocarp [22].

Paracetamol (also known as acetaminophen) is one of the pharmaceuticals of common use worldwide due to its effectiveness in the relief of pain and fever. Paracetamol is easily accumulated in the aquatic environment due to its relatively high solubility and hydrophilicity. Moreover, it has been confirmed that 58%–68% of paracetamol and its metabolites are excreted from the body during therapeutic use [23,24]. Paracetamol is not a biodegradable pharmaceutical product,

hence it does not decompose easily in the environment [1]. Paracetamol is a relatively safe drug but toxic side effects have been observed with high doses greater than 10–15 g. This toxicity is due to the chemical structure of the compound and the way the human body breaks it down. It is metabolized to a reactive intermediate at high doses [25]. Paracetamol stands out for being highly toxic to the liver [26,27], with a potential risk of hepatitis development [27]. In order to avoid serious disturbances in aquatic life, efficient and economically viable procedures should be developed for removing common pollutants, like paracetamol.

Ribeiro et al. [28] evaluated the efficiency of two natural adsorbents (vegetable sponge and sugarcane bagasse) for the removal of paracetamol dispersed in aqueous solutions. In this study, a glass column was used to conduct the experiments at a pH of 7 and the adsorption isotherm parameters were calculated for both adsorbent materials. Sugarcane bagasse gave more attractive results than vegetable sponges in terms of price and efficiency of removal. Also, sugarcane bagasse has a larger number of pores than vegetable sponges. Mohd et al. [29] investigated the performance of activated carbon and modified cellulose on the adsorption of paracetamol from an aqueous solution using the batch method. Higher percentage removal was achieved at the acidic range and higher temperature (that is, spontaneous and favorable); the equilibrium data fitted well with the Langmuir model with a correlation coefficient, R^2 of 0.9522. Mashayekh-Salehi and Moussavi [30] investigated the efficiency of NH_4Cl -induced activated carbon on the removal of paracetamol; the adsorption kinetic data followed the pseudo-second-order kinetic model. These studies showed that the choice of adsorbent material influences the adsorption of paracetamol.

Olivine is a naturally abundant mineral rich in magnesium, silica, and iron with the chemical formula: $(\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4$ [31]. Olivine is recognized as a mineral group with the forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4) end members. Fayalite and forsterite create a solid solution series, and most specimens identified as olivine fall somewhere in between this series. Olivine incorporates only minor amounts of elements other than oxygen, silicon, magnesium, and iron. Manganese and nickel are the commonly additional elements present in the highest concentrations. Olivine is named for its typically olive-green color (thought to be a result of traces of nickel), though it may alter to a reddish color from the oxidation of iron. This sandy material is mechanically hard and attrition resistant, which made it acceptable as a potential support material in the field of catalysis [32]. Olivine has several industrial uses; it is used as a flux for steel production and is also an important ore of the magnesium metal. The application of olivine to water treatment has not been explored so far. It was used to treat synthetic acidic mine water because olivine is a basic mineral and can bind more acid per unit volume [33]. Olivine was also utilized for the removal of arsenic from water [34].

The goal of this study is to determine the effectiveness of the adsorbent material, olivine for the removal of paracetamol from water in the presence and absence of ultrasonic waves. To the best of our literature search, this adsorbent material has never been utilized for this particular pollutant (paracetamol). Even the Fourier-transform infrared spectroscopy (FT-IR) detection technique has not been used

to determine the concentration of pollutants after olivine utilization for the treatment of polluted water. Therefore, this research tends to fill this gap, hence, the novelty of the present study. The thermodynamics of the process was considered. The effect of ultrasonic waves on the adsorptive removal of paracetamol was investigated. Also, the kinetics of the removal process was demonstrated with and without ultrasonic waves.

2. Experimental

2.1. Materials

The olivine with the crystal structure shown in Fig. 1 [29] was collected from Tafila, South Jordan. It was crushed, milled, dried overnight, and then taken for scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) analysis. This was done through SEM equipment (QUANTA INSPECT F50, FEI Company, Eindhoven, The Netherlands). The particles of olivine that passed through the 150 μm sieve and were retained on the 45 μm sieve were used. Paracetamol (99% purity) (Fig. 2) was obtained from a local pharmaceutical company in South Jordan. The wastewater was prepared by dissolving 10 g of paracetamol in 2 L of distilled water.

2.2. Batch experiments

Batch sorption experiments were conducted in a series of 250-mL glass beakers containing 100 mL of 5.0×10^3 ppm paracetamol solution. 0.5 g of olivine ($<0.05 \mu\text{m}$) was mixed with the paracetamol solutions and continuously stirred with magnetic stirrers for a specified time at a particular temperature with (at a constant ultrasonic frequency of 37 kHz) or without ultra-sonication. After the completion of the experiments, the samples were filtered and the percentage of paracetamol removed was determined. The olivine was washed with distilled water and dried

overnight for infrared (IR) analysis. The FT-IR analysis ($4,000\text{--}400 \text{ cm}^{-1}$, 4 cm^{-1} spectral resolution, KBr pellets) was done using a Thermo Nicolet NEXUS 670 FT-IR spectrometer (Massachusetts, United States). The standard calibration curve for paracetamol analysis was established based on IR measurements by mixing a precisely weighed amount of paracetamol (0.0, 0.01, and 0.05 g) with 0.5 g of olivine. The concentration of paracetamol was calculated using a calibration curve that was plotted based on IR measurements. The removal percentage of paracetamol was calculated using the following equation [35]:

$$\text{Removal}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are the initial and final concentrations (mg L^{-1}) of paracetamol in solution, respectively. These concentrations of paracetamol were measured through the IR analysis by taking measurements of the IR band height of the transmitted bands and calculating the final concentration of paracetamol solution using a regression equation obtained from the plot of IR band height vs. the concentration of paracetamol (calibration plot). The band height/transmittance was plotted against the wavelength (FT-IR spectra) at paracetamol amounts of 0.0, 0.01, and 0.05 g to determine if the IR analysis can be used as a method for the determination of paracetamol concentration in water. All experiments were done twice.

2.3. Thermodynamics analysis

Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were calculated from the variation of the thermodynamic equilibrium constant (K) with the temperature (T). Gibb's free energy (ΔG°) can be calculated from the thermodynamic equilibrium constant (K). The adsorption standard free energy

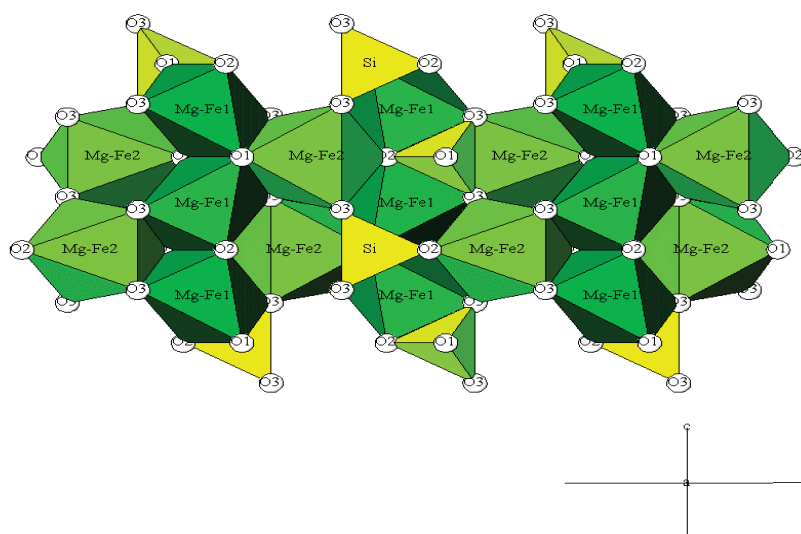


Fig. 1. Crystal structure of olivine.

changes (ΔG°) can be calculated according to the following equation [36]:

$$\Delta G^\circ = -RT \ln K \quad (2)$$

where R is the universal gas constant ($8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$) and T is the temperature in Kelvin.

The enthalpy (ΔH°) and entropy (ΔS°) of the adsorption process were calculated using the following Van't Hoff's equation [37]:

$$pK = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (3)$$

The value of enthalpy (ΔH°) was calculated from the slope, and the value of entropy (ΔS°) was obtained from the intercept of the plot of pK ($=-\log K$) vs. $1/T$.

3. Results and discussions

3.1. Characterization of olivine

The SEM-EDX spectrum is presented in Fig. 3. The scanning electron microscopy (SEM) was carried out to

determine the surface morphology of the olivine under an acceleration voltage of 15 kV. Very rough surface and sharp edges can be observed on the SEM image of olivine (at 400X) (Fig. 3). The pores observed on the adsorbent material (Fig. 3) will lead to significant adsorption sites for the adsorbate, paracetamol. The presence of silicon and oxygen confirms the high purity of the material [38]; these elements can also be confirmed in the structure of olivine displayed in Fig. 1.

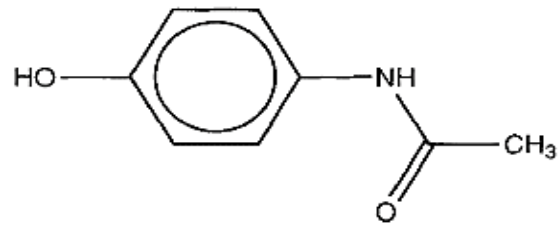


Fig. 2. Paracetamol chemical structure.

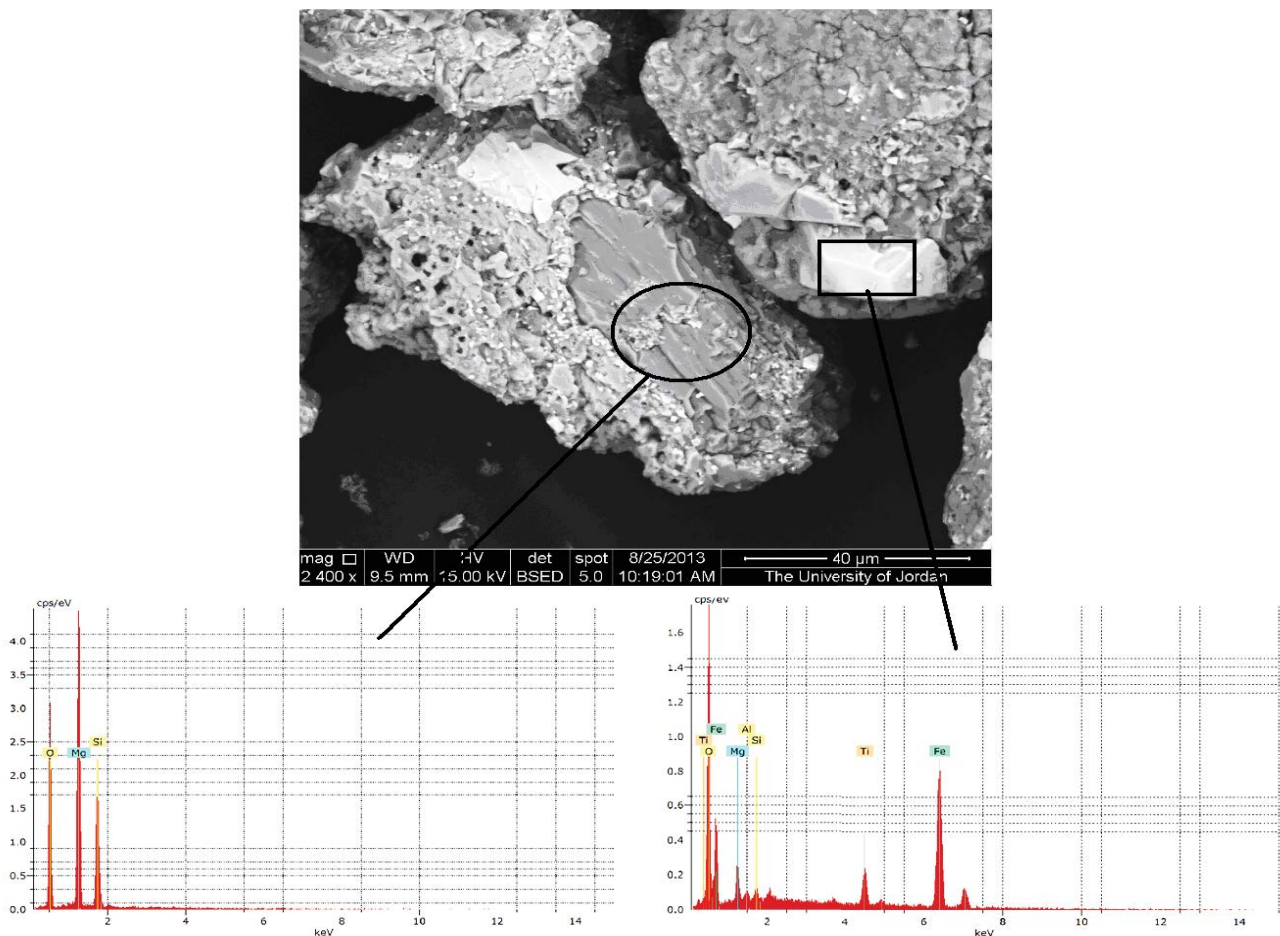


Fig. 3. SEM-EDX spectrum of olivine.

3.2. Adsorption studies

3.2.1. Removal of paracetamol

IR spectrum was obtained for three different amounts of paracetamol (0.0, 0.01, and 0.05 g) with 0.5 g of olivine (Fig. 4). The height of the transmitted bands was plotted vs. the amount of paracetamol as seen in Fig. 4. The spectra at 0.0 g paracetamol are that of the pure olivine (Fig. 4a). It is obvious that the height of all transmittance bands increased as the amount of paracetamol in the solution was increased to 0.01 and 0.05 g, which means that IR is one of the methods that can be used for the determination of paracetamol concentration. Based on Fig. 4b and c, the broad transmittance bands at 3,600 and 3,438 cm^{-1} are assigned to the OH and NH stretching vibrations in paracetamol, which also can be seen in the structure of paracetamol (Fig. 2). Paracetamol is known to have functional groups of hydroxyl, amide groups, and aromatic groups [39]. The OH vibration was also observed on the pure olivine (Fig. 4a), that is at 0.0 g paracetamol. The bands above 2,511 cm^{-1} are attributed to the stretching vibrations of the methyl group (Fig. 4a–c). The vibrations in the range of 1,682–1,530 cm^{-1} are due to the stretching vibrations of the phenyl ring. The intense 1,683 and 1,753 cm^{-1} band of a paracetamol solution (Fig. 4b and c) corresponds to the first band of the amide group, reflecting the state of the C=O bond; which is also present in Fig. 4a. The vibrations in the range of 1,291–950 cm^{-1} (Fig. 4a–c) are in-plane deformation vibrations of the C–H bonds of the phenyl ring, which are mixed with the stretching and deformation vibrations of the amide fragment [40]. Another existing bond is the C–C stretch of aromatics (625 cm^{-1}) [41]. Paracetamol's OH and NH groups can operate as strong electron donors, causing the aromatic ring to increase electron density [9]. The amide group in ACT, in particular, is an aromatic ring activating group in which molecule electrons interact with delocalized adsorbent electrons [42]. The primary mechanism controlling paracetamol adsorption, according to several researchers, is the π – π interactions [9]. The spectra (Fig. 4) revealed that the olivine containing paracetamol particles (Fig. 4b and c)

contained more functional groups than the pure olivine with 0.0 g paracetamol particles (Fig. 4a), owing to the addition of more functional groups present in the paracetamol. Some functional groups were common to all, with the exception that the height of all transmittance bands for pure olivine was raised when paracetamol was added.

Fig. 5 illustrates the constructed calibration curve (IR band height vs. paracetamol concentration) for measuring the concentration of paracetamol based on the height of IR transmittance bands.

In order to investigate the effect of ultrasonic waves on the removal process of paracetamol on olivine, the concentration of paracetamol was determined with time using IR spectroscopy. The change in IR spectra of paracetamol with time was considered with ultrasonic waves and without ultrasonic waves (Fig. 6). As time increases, the height of the band increases which indicates the increasing amount of paracetamol introduced to the system. Ultrasonic waves also caused a shift in the peak at 1,750 cm^{-1} for the spectra in Fig. 6. Also, the height of the transmittance at 1,500 cm^{-1} was increased in the presence of ultrasound. Fig. 7 shows the change in paracetamol amount in grams with time under the condition of ultrasonic waves compared to without ultrasonic waves. The rate of change in concentration with time increased in the absence of ultrasonic waves but decreased steeply in the presence of ultrasonic waves.

A similar trend is shown in Table 1 which illustrates the paracetamol percentage removal with time considering the effect of ultrasonic waves on the adsorption process. From Table 1, it is obvious that the paracetamol removal percentage was increased with ultrasonic waves at the same time. The combined effects of adsorption and sonolytic degradation enhanced the rate of change in paracetamol concentration in the presence of ultrasonic waves [43]. Ultrasound waves enhanced the mass transport in the pores of the olivine adsorbent [44]. Also, the removal of paracetamol was increased simultaneously as the adsorption time was increased in the presence of ultrasonic waves. This phenomenon is due to enough time allowed for the process to take place [45]. However, in the absence of ultrasonic waves, the elimination of paracetamol

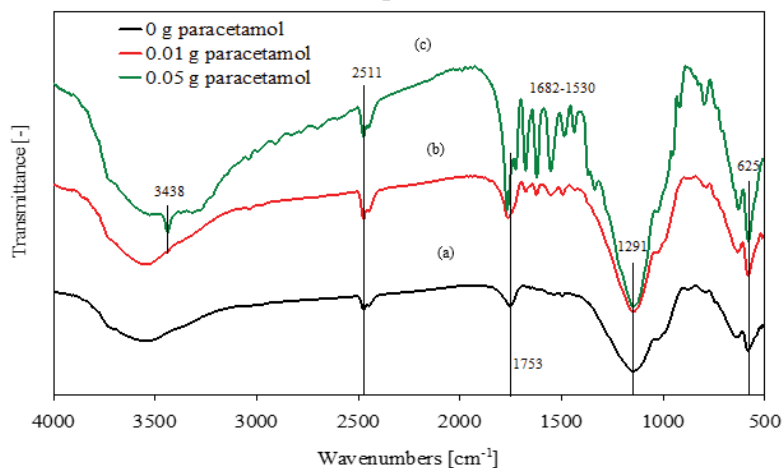


Fig. 4. IR spectra of paracetamol at three different amounts (0, 0.01, and 0.05 g) with 0.5 g of olivine.

reduced concurrently as the reaction time rose; this means that desorption happened [46].

3.2.2. Thermodynamics of adsorption

Fig. 8 is the plot of pK ($=-\log K$) vs. $1/T$. The calculated values of thermodynamic parameters for paracetamol removal using olivine are presented in Table 2. The exothermic nature of adsorption was clearly shown by the

negative value of ΔH° ($-2.674 \text{ kJ mol}^{-1}$) which is also governed by the possibility of chemical adsorption. The positive values of ΔG° (2.272 to $2.075 \text{ kJ mol}^{-1}$) indicate the non-spontaneity and the unfavorability of the removal of paracetamol on olivine; this also implies that the process of paracetamol adsorption on olivine does not require higher temperatures and denotes random feasibility [47]. Similar non-spontaneous behavior was observed by Ferreira et al. [1] and Ismael et al. [48] for paracetamol removal. Also,

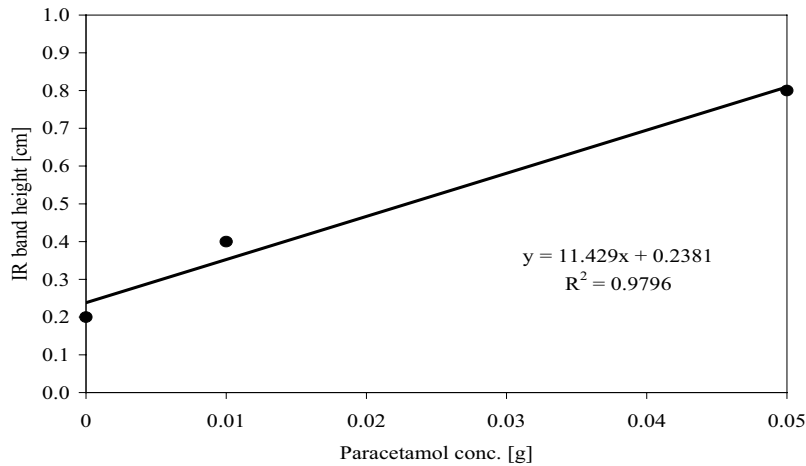


Fig. 5. Calibration curve of paracetamol.

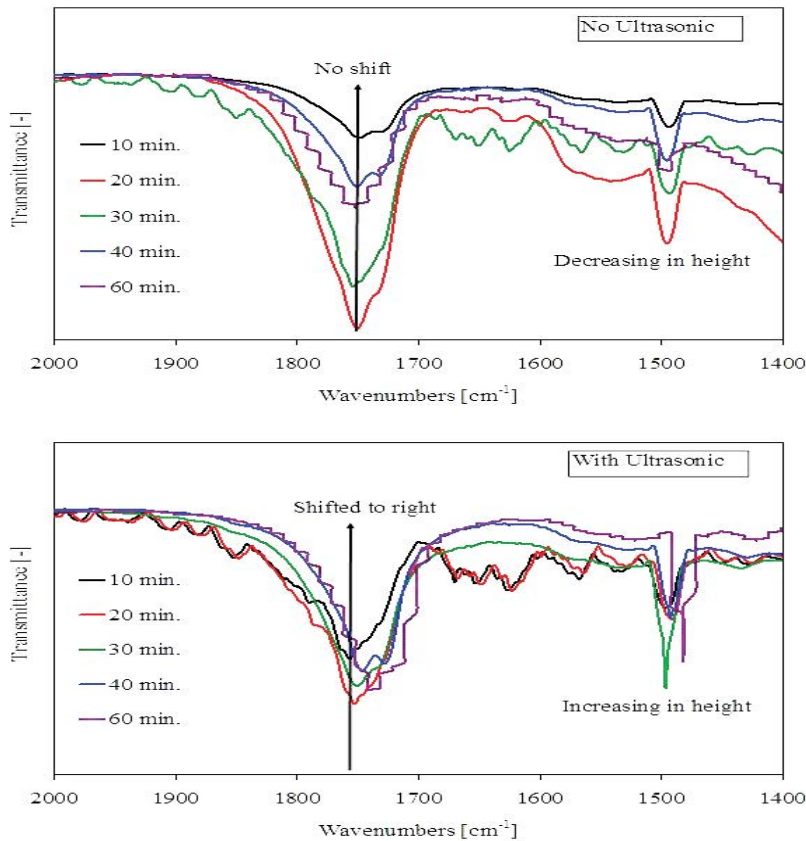


Fig. 6. IR spectra of paracetamol with time with no ultrasonic waves and with ultrasonic waves.

external influence/force is required to navigate this process [14]. The existence of chemical bonds is suggested when ΔG° (the free energy) $>40 \text{ kJ mol}^{-1}$ and it is physisorption when $\Delta G^\circ < 40 \text{ kJ mol}^{-1}$ [9]. For this study, the prevailing process is physisorption (Van der Waal's forces and hydrogen bonding) since $\Delta G^\circ < 40 \text{ kJ mol}^{-1}$. This also implies that organic solvents or distilled water may elute paracetamol from the olivine sorption surface. The negative value of

ΔS° ($-0.0969 \text{ kJ mol}^{-1}$) shows the decreased disorderliness adsorbent [49].

3.2.3. Kinetics of adsorption

Kinetic studies were conducted to determine the mechanism of the adsorption of paracetamol on olivine. The rate of paracetamol adsorption on olivine was studied by measuring the change in concentration as a function of time. The volume of solution, mass of adsorbent, and initial concentration were kept constant. The removal rate of paracetamol by olivine can be evaluated by studying adsorption kinetics. The optimum contact time for an adsorption process can also be obtained from such studies. At the beginning of the adsorption process, the rate of removal was high due to the availability of adsorption sites on the adsorbent surface. The nature, surface area, and amount of adsorbent affect the kinetics of the adsorption process. The kinetics of paracetamol adsorption on olivine were analyzed by calculating the amount of paracetamol adsorbed with time. The uptake of paracetamol molecules was calculated from the mass balance, which was stated

Table 1
Percentage of removal of paracetamol from the solution under the condition of ultrasonic waves

Time (min)	Removal (%)	
	No ultrasonic	With ultrasonic
10	–	–
20	28.56 ± 0.99	30.05 ± 1.07
30	19.99 ± 1.13	79.98 ± 1.41
40	11.42 ± 1.26	88.55 ± 1.16
60	–	97.12 ± 0.28

Table 2
Thermodynamic parameters of paracetamol removal by olivine

Temperature (°C)	Removal (%)	K (mol dm ⁻³)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)
25	28.5	0.400	2.272		
40	21.7	0.277	3.179	-2.674	-0.0969
48	16.6	0.198	4.006		
60	11.4	0.129	5.075		

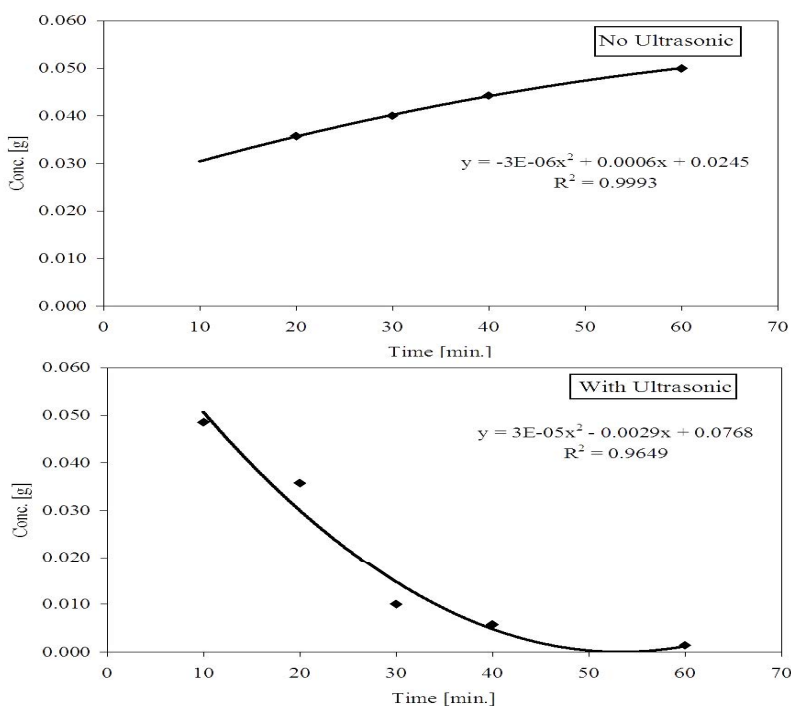


Fig. 7. Change in paracetamol amount in grams with and without ultrasonic waves.

as the amount of solute adsorbed onto the solid. It is equal to the amount of solute removed from the solution. For the kinetic studies, paracetamol concentration was calculated every 10 min for 1 h. The adsorbed amount (Q_e) per unit adsorbent mass (mg g^{-1}) was calculated according to Eq. (4) [50]:

$$Q_e = \frac{(C_0 - C_e)V}{m} \tag{4}$$

where C_0 is the initial concentration of adsorbate, C_e is the concentration of the substrate at equilibrium (mg dm^{-3}), m

is the adsorbent mass (mg) and V is the solution volume (dm^3). Such calculations were performed with- and without the condition of ultrasonic waves. The intraparticle diffusion kinetic model (Eq. (5)) [36,51] is shown below as used to make the plots.

$$Q_e = K_i t^{0.5} + c_i \tag{5}$$

where K_i is the intra-particle diffusion rate constant (mg (g min)^{-1}) and c_i is the intercept (mg g^{-1}) which may be evaluated from the plots of Q_e vs. $t^{0.5}$.

Fig. 9 shows the plot of Q_e vs. $t^{0.5}$. Based on Fig. 9, it is clearly obvious that the amount of paracetamol adsorbed

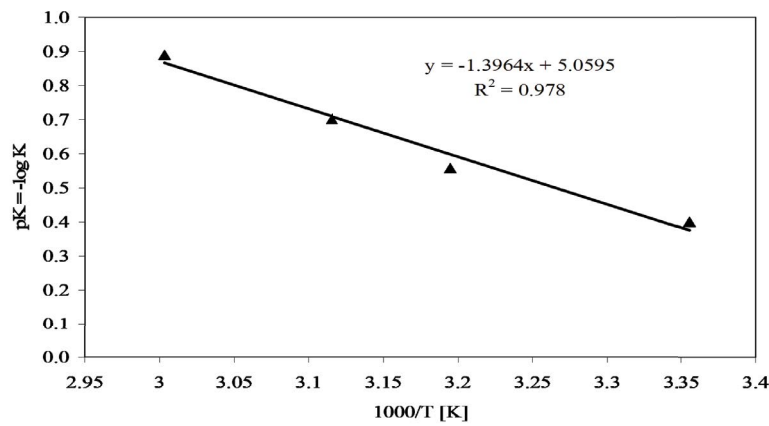


Fig. 8. Plot of pK vs. 1,000/T for paracetamol removal by olivine.

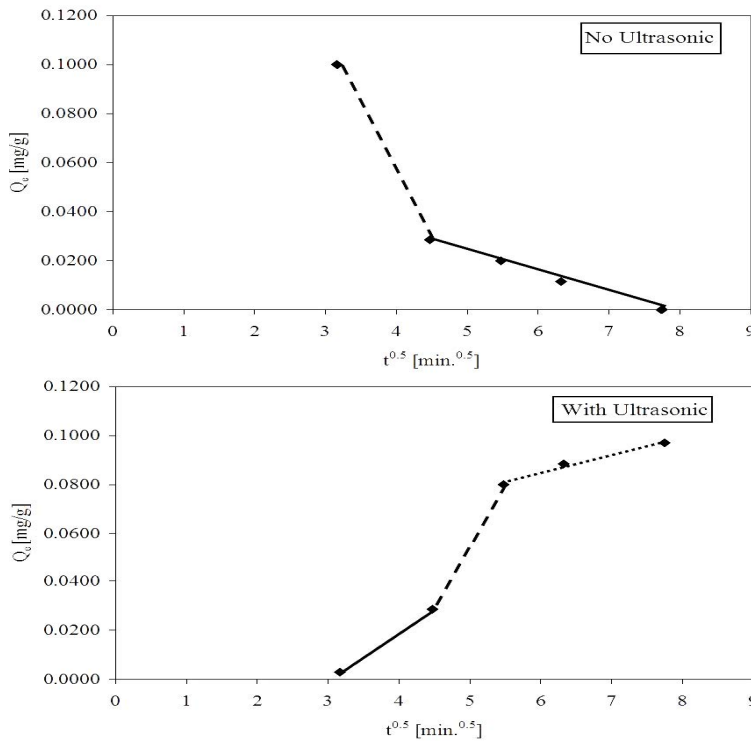


Fig. 9. Plot of Q_e (concentration of the paracetamol at equilibrium) vs. $t^{0.5}$ with and without ultrasonic waves.

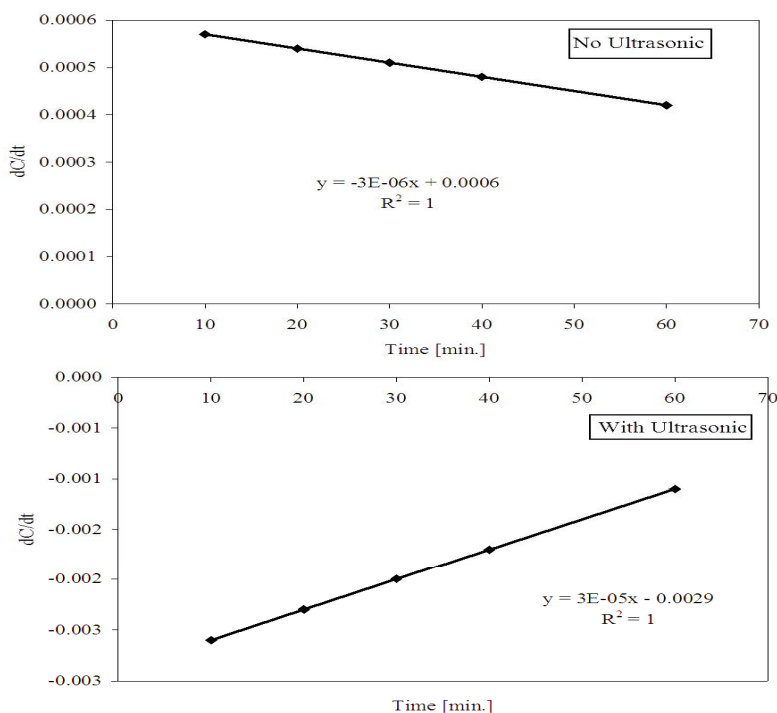


Fig. 10. Change of paracetamol concentration with time with and without ultrasonic waves.

was significantly improved in the presence of ultrasonic waves at all studied times of contact. When pore diffusion restricts adsorption, the rate of adsorption will not be linear [52]. Since the results reveal multi-linear plots (Fig. 9) as predicted by Weber and Morris, the adsorption process must entail two or more stages [53,54]. Two (no ultrasonic) or three (with ultrasonic) stages are depicted in the plots (Fig. 9). All of the stages were rapid and demonstrated decreased or increased adsorption respectively for no ultrasonic and with ultrasonic, respectively as a result of the boundary layer diffusion [54,55].

Change in paracetamol concentration in solution was also recorded with time and plotted as shown in Fig. 10. Fig. 10 depicts that the adsorption rate (change in concentration with time) was increased in the presence of ultrasonic waves. The rate of adsorption decreased when the process was carried out in the absence of ultrasonic. The increase in the rate of adsorption in presence of ultrasonic waves is owing to the combined effects of adsorption improvement and sonolytic degradation [43] whereby ultrasound waves enhanced the mass transport/adsorption velocity in the pores of the olivine adsorbent [44].

4. Conclusion

Natural olivine from Jordan is capable of removing paracetamol from aqueous solutions. The influence of temperature, contact duration, and ultrasonic waves at a frequency of 37 kHz on paracetamol removal was studied. The kinetics data were collected under normal and ultrasonic circumstances. The percentage of paracetamol eliminated increased as the time spent in the presence of ultrasonic waves increased (with maximum removal of

97.12% at 60 min and 0.5 g of olivine). Paracetamol adsorption was found to be unfavorable and non-spontaneous (with ΔG° ranging from 2.272 to 5.075 kJ mol⁻¹), and as well as exothermic ($\Delta H^\circ = -2.674$ kJ mol⁻¹). The process was also observed to be physisorption in nature the combined effects of adsorption with ultrasonic waves enhanced the quantity of paracetamol adsorbed (Q_e) in the kinetics investigations. Ultrasound waves enhanced the mass transport in the pores of the olivine adsorbent.

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