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Kinetic Behavior of the Adsorption of Malachite Green Using Jordanian Diatomite as Adsorbent

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Chemical Engineering Department, Mu’tah University, Karak, 61710 Jordan

The main intention of this work is to study the adsorption rate and mechanism for the adsorption of Malachite Green dye (MG) onto Jordanian diatomite. A series of experiments were conducted under a variety of conditions such as the mass of diatomite, initial MG concentration, and pH of the solution. The mechanism of adsorption was elucidated based on different kinetic models. Experimental conditions showed a considerable effect on the adsorption rate. Alkali conditions promote MG uptake and increase the rate of adsorption. Approximately 99% of dye removal was achieved as the diatomite dosage increased from 0.25g to 1.5g. The adsorption rate-controlling step was found to be a combination of chemisorption and intraparticle diffusion, with the external mass transfer predominating in the first five minutes of the experiment.

Keywords: Adsorption; Malachite green; Diatomite; Kinetic model; Biot Number.

Introduction

Elimination of dyes from wastewater is vitally an important environmental issue and has to gain attention. Adsorption technology is considered as a powerful and promising treatment technique for a wide range of pollutants including dyes (Hasanzadeh *et al*., 2019; Georgiadis *et al*., 2013; Sartape *et al*., 2017; Dhahir *et al*., 2013). Generally, three consecutive steps are involved in the solid-liquid adsorption process and include (Lazaridis and Asouhidou, 2003; Nethajia *et al*., 2010): i) Boundary layer or film diffusion: pollutant is transferred from the bulk solution through the liquid film to the exterior surface of the adsorbent; ii) Intraparticle diffusion: diffusion of pollutant into the pore of adsorbent or sorption on the external surface; and iii) Adsorption at a site: adsorption of pollutant on the interior surfaces of pores and capillary spaces of the adsorbent.

Since the third step is generally very rapid compared to the first and the second step, the adsorption processes are usually controlled by either film or intraparticle diffusion or both (Nethajia *et al*., 2010). If the external transport is greater than the internal transport, the adsorption process is controlled by intraparticle diffusion. Whereas if the external transport is less than internal transport, the adsorption process is controlled by film diffusion. When the external transport is almost equal to the internal transport, the transport of the pollutants to the boundary may not be promising at a significant rate (Mittal, 2006).
The knowledge of the adsorption capacity and adsorption rate is of paramount importance to gain a better understanding of the adsorption process. Even though equilibrium studies determine the maximum adsorption capacity of the adsorbent and very helpful in determining the efficiency of the adsorption process, the efficiency is also strongly dependent on the adsorption system’s kinetics (Regazzoni, 2019; Krishnan and Anirudhan, 2002; Rudzinski and Plazinski, 2001).

Furthermore, adsorption kinetics is of paramount importance when designing adsorption systems. It helps the designer to select the appropriate adsorbent and applying it correctly. The kinetic study is also of crucial importance in determining the mechanism of the adsorption process and provides valuable information regarding the adsorption rate and the factors affecting the adsorption rate (Guo and Wang, 2019; Pan and Zhang, 2009).
Many investigators have reported the significance of the adsorption kinetics (Sartape *et al*., 2017; Arivoli *et al*., 2009; Pan and Zhang, 2009; Hema and Arivoli, 2008; Ho, 2006). Thus, a deep understanding of the adsorption kinetics is essential to assess the performance of the adsorption system. Equilibrium aspects of the adsorption of MG onto Jordanian diatomite have been studied and discussed.

Detailed information about the equilibrium study is well documented in (El Qada, 2019). However, the adsorption kinetics of the Jordanian diatomite-MG adsorption system has not been reported in the literature (Alali, 2015). Therefore, as a continuation of the equilibrium study and to complete the adsorption process aspects of MG onto Jordanian diatomite, the present study is intended to understand the mechanism of the transport processes that govern the removal of MG from aqueous solution and the parameters affecting the adsorption rate.

Received on September 2, 2019; accepted on November 16, 2019 Correspondence concerning this article should be addressed to Emad. El Qada (E-mail address: e_anadele@yahoo.com ORCiD ID of Emad El Qada https https://orcid.org/0000-0002-3364-8618.

1 Materials and Methods

1.1 Materials:

Malachite Green dye ($C_{23}H_{25}N_2Cl$) and Jordanian diatomite were used in this study as adsorbate and adsorbent, respectively. More information about them is reported elsewhere (El Qada, 2019).

1.2 Kinetic Adsorption:

Several kinetic adsorption experiments were conducted to investigate the rate and mechanism of MG adsorption onto Jordanian diatomite. The effect of pH, initial dye concentration, and diatomite mass was studied to assess the time dependence of the adsorption process. An agitated glass beaker of the internal diameter of 0.13m and with a capacity of 2 dm^3 solutions was used. The beaker was equipped with four-blade glass impellers driven by the electric motor to stir MG solution and diatomite. Four baffles were fixed evenly around the circumference of the adsorber to ensure complete mixing and preclude vortex formation during the experiment. The progress of MG adsorption was determined by measuring the absorbance of the MG at different time intervals using Varian Cary-50 UV/VIS spectrophotometer (USA). All the kinetics experiments were performed at room temperature.

The amount of MG adsorption at the time, t, was calculated using Eq. (1):

$$q_t = \frac{(C_o - C_t)V}{m} \tag{1}$$

where q_t is the amount of MG adsorbed at time t (mg/g); C_o is the initial dye concentration (mg/ dm^3), C_t is the concentration of MG solution at time t, (mg/ dm^3); m is mass of the diatomite (g) and V is the volume of MG solution (dm^3). Table 1 lists the experimental conditions used in performing kinetics adsorption experiments. The kinetic data were then analyzed by fitting it to different kinetic models in an attempt to elucidate the rate and adsorption mechanism of MG onto Jordanian diatomite. Out of several kinetic models available, the most common ones namely, external mass transfer model, pseudo-second-order kinetic model, intraparticle diffusion model, Boyd model, and Elovich model were used. Transport numbers and Biot numbers were also utilized. The applicability of the kinetic models was compared by judging the regression coefficients, r^2.

Table 1 Experimental conditions of adsorption kinetics.

Initial dye concentration (ppm)	Particle size (µm)	Mass of adsorbent (g)	pH of dye solution
25	500-710*	0.25	5.00
50	250-500	0.50	7.00*
100*	25-250	0.75*	9.00
150	---------	1.50	11.0

** Standard conditions*

2 Results and Discussion

2.1 Effect of Solution pH:

To study the effect of pH on the adsorption kinetics of MG onto Jordanian diatomite, different values of MG solution pH were prepared (5-11). The result of the pH effect on the adsorption of MG from aqueous solution is shown in **Figure 1**. The MG uptake is seen to be favored at the basic condition. A significant increase in the adsorption rate is noticeable at the higher values of solution pH. MG uptake was increased from 110 mg/g to 182.5 mg/g in 20 minutes as the pH increased from 5 to 11. Besides, the adsorption efficiency was increased from 62.8 % to 98.5% for an equilibrium time of 45 min. This indicates that solution pH plays an essential role in the adsorption process. As the solution pH was changed from the acidic range to the alkaline range, the diatomite surface became negatively charged which in turn promoted the adsorption of the positively charged dye (MG) and thus increased the rate of the adsorption process. These results agree well with previously reported results on the adsorption of MG onto organoclay (Ullah *et al*., 2017). Moreover, another study (Song *et al*., 2015) supports these findings. Hence, they found that by lowering the solution pH, the amount MG sequestered from the solution was reduced and they attributed this trend to the neutralization effect of excess H^+ ions present in the acidic medium which neutralizes the negative charge at the surface of the

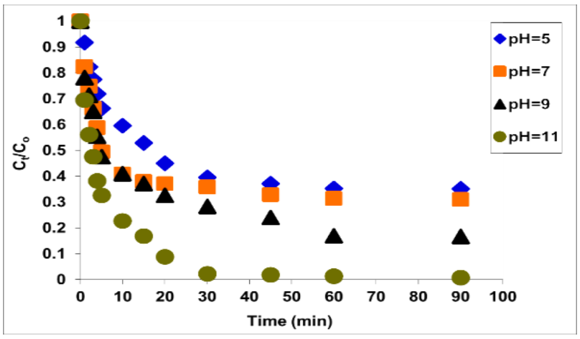

Fig. 1 Effect of solution pH on the adsorption rate of MG onto diatomite, concentration 100 ppm, agitation agitation 300 rpm, temperature 25ºC, size 500-710µm, mass 0.75g, and volume 1.7 dm^3

adsorbent. Increasing solution pH usually reduce the protonation process and supply more vacant negatively charged adsorption sites required for the adsorption of cationic dye.

2.2 Effect of Initial Dye Concentration:

It is well-recognized in the adsorption field that the initial dye concentration plays a significant role in controlling the rate of the adsorption process. For a better understanding of this role, various initial dye concentrations (25, 50, 100 and 150 ppm) were utilized in different kinetic experiments. **Figure 2** depicts the effect of the initial MG concentration on the adsorption rate of the MG-diatomite system. The kinetic data reveals that there is a direct relationship between the adsorption capacity and the initial dye concentration. The adsorption capacity was increased. This is consistent with the results obtained previously (Song *et al.*, 2015; Chiou and Li, 2002; Santhi *et al.*, 2015). On the contrary, the percentage removal of MG from the aqueous solution was dropped from 99.9% to 66.4% as the initial MG concentration increased from 25 ppm to 150 ppm. Another study reported a similar trend and suggested that there is a fixed number of adsorption sites, so at low initial dye concentration, few dye molecules will be available which can easily access a higher number of the available adsorption sites and this, in turn, raise the adsorption efficiency (Ullah *et al.*, 2017). This quantity of accessible sites is less in the case of higher dye concentration because of the competition between dye molecules for the fixed number of adsorption sites, thus some of the dye molecules did not get absorbed and remain in the solution causing the reduction in the adsorption efficiency. It is also evident that more time is required to reach the equilibrium state at higher initial MG concentrations. 15 minutes were enough to reach equilibrium in the case of 25 ppm solution, whereas 45 minutes were required for the 150-ppm solution. The higher the initial MG concentration, the slower the decrease in the dimensionless concentration (C_t/C_o). At high initial dye concentration, more MG molecules are available in the system which means strong competition between MG for the available adsorption sites.

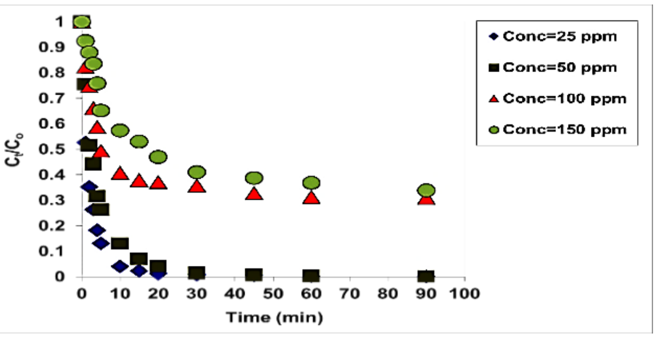

Fig. 2 Effect of initial dye concentration on the adsorption rate of MG onto diatomite. Mass 0.75g, agitation 300 rpm, temperature 25°C, size 500-710µm, mass 0.75g, pH 7, and volume 1.7 dm^3

2.3 Effect of the mass of adsorbent

Different kinetic adsorption experiments were performed to study the effect of diatomite concentration on the removal of MG from aqueous solution. Different masses of diatomite ranging from 0.25-1.500 (g) were used. Other experimental factors were kept constant. The effect of the diatomite concentration on the removal of MG is reported in **Figure 3**. It can be observed from Figure 3 that there is a direct proportionality between the rate of the adsorption and the concentration of diatomite. The removal efficiency at equilibrium increased from 44.2% to 99.36% when the diatomite dose was increased from 0. 25 g to 1.5 g. The opposite trend was obtained for the adsorption capacity. Diatomite adsorption capacity was decreased from 176.8 mg/g to 99.35 mg/g as the diatomite dose increased from 0. 25 g to 1.5 g. The increase in the adsorption efficiency can be explained by the increase in the binding sites available on the adsorbent surface at a higher dosage of diatomite (Shirmardi *et al.*, 2013). While the decrease in diatomite capacity can be attributed to the fact that increasing the diatomite dose and fixing the dye concentration resulted in unoccupied adsorption sites at higher dosages of diatomite and thus reducing the diatomite adsorption capacity (Ullah *et al.*, 2017). It is also clear that by increasing diatomite dose the curve becomes steeper which means a faster rate of adsorption. Numerous studies have been mentioned that by increasing the adsorbent dosage, the adsorption rate increases (Litefti *et al.*, 2017; Aazza *et al.*, 2017; Sawasdee and Watcharabundit, 2015). Besides, the obtained kinetics results showed that high adsorption rates were attained in the first five minutes followed by gradual removal at a lower rate until equilibrium. This behavior can be attributed to the rapid attachment of MG on the surface of diatomite within the first five minutes. Thereafter, the diatomite surface was saturated by MG molecules and the dye molecules start to diffuse through

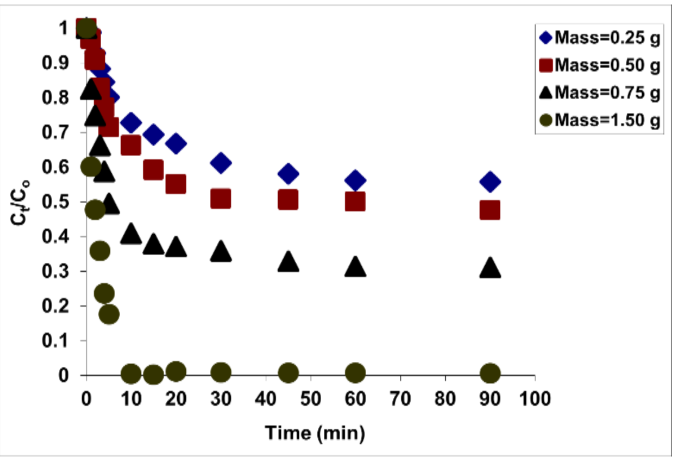

Fig. 3 The effect of diatomite concentration on the adsorption rate of MG onto diatomite. Temperature 25°C, size 500-710µm, concentration 100 mg/dm^3, pH7, agitation 300 rpm and volume 1.7 dm^3.

the pores (intraparticle diffusion). Results reported in (Sawasdee and Watcharabundit, 2015) illustrated that the rapid dye removal in the initial stage is due to the abundant availability of active sites on the adsorbents surface, once these sites are gradually occupied, the adsorption process became less efficient. On the other hand, another study (Benmaamar *et al*., 2016), attributed the slower gradual removal of dye molecules after the lapse of time to the repulsion forces between the dye molecules adsorbed on the solid and dye molecules in the liquid phase which makes it took a long time to reach equilibrium.

2.4 Adsorption Kinetics Modelling

2.4.1 Furusawa-Smith Model

To explore the significance of the external mass transfer resistance on the adsorption rate of MG onto Jordanian diatomite, the Furusawa-Smith model was utilized. The model depicts the relation between the mass transfer coefficient and the change in the liquid phase concentration with time. High values of external mass transfer coefficient usually reflect low resistance to the mass transfer experienced by the adsorbate as it transfers from the liquid phase to the solid phase. The mass transfer coefficient was determined using the linearized form of Furusawa-Smith model (Furusawa, and Smith, 1973):

$$Ln\left(\frac{C_t}{C_o}-\frac{1}{1+m_s k_L}\right)=Ln\left(\frac{m_s k_L}{1+m_s k_L}\right)-\left(\frac{1+m_s k_L}{m_s k_L}\right).k_f S_s t \quad (2)$$

where C_t is the liquid-phase concentration at time t (mg/dm^3); C_o is the initial phase concentration (mg/dm^3); k_L is a Langmuir constant (dm^3/g); m_s is the concentration of adsorbent (g/dm^3); S_s is the specific surface area (m^{-1}); t is the time (min), and k_f is the external mass transfer coefficient (m.min^{-1}).

Table 2 External mass transfer coefficient for the adsorption of MG onto diatomite.

Variable pH	K_f x10^3 (m.min^{-1})	r^2	Conc. (ppm)	K_f x10^3 (m.min^{-1})	r^2	Mass (g)	K_f x10^3 (m.min^{-1})	r^2
5	1.748	0.9960	25	11.80	0.9200	0.25	1.482	0.9840
7*	2.212	0.9900	50	5.081	0.9930	0.500	1.599	0.9840
9	2.540	0.9960	150	1.283	0.9480	1.500	3.015	0.9900
11	3.272	0.9950	-------	-------	--------	-------	--------	--------

** Standard experimental conditions, concentration 100 ppm, pH 7, agitation 300 rpm, particle size 500-710 µm and mass 0.75 g.*

Table 2 lists the values of the external mass transfer coefficient, k_f, for the adsorption of MG onto diatomite. The obtained results showed that increasing diatomite mass has led to a decrease in the external mass transfer resistance as can be seen from the increases in the k_f values. Thus, the rate of MG adsorption onto diatomite was increased. Besides, increasing the solution pH also caused an increase in k_f value and hence a decrease in the external mass transfer resistance. These findings are similar to other research results (Mckay *et al*., 1986). They illustrated that increasing adsorbent dosage will increase turbulence from the particles which in turn will increase the mobility of the adsorbate and facilitate their crossing through the boundary layer to the particle surface. An opposite trend was observed with the increase in the initial MG concentration. The mass transfer coefficient decreases as the initial MG concentration increases. Hence the initial rate of adsorption was decreased. This is probably due to the interactions between MG molecules in the solution and the competition for the available adsorption sites overriding the increase in the driving force and at higher MG concentration (Girish and Murty, 2016). **Figure 4** displays the application of the Furusawa-Smith model to the experimental data for the adsorption of MG onto diatomite at different adsorbent masses. The results show that the Furusawa-Smith model was able to predict the

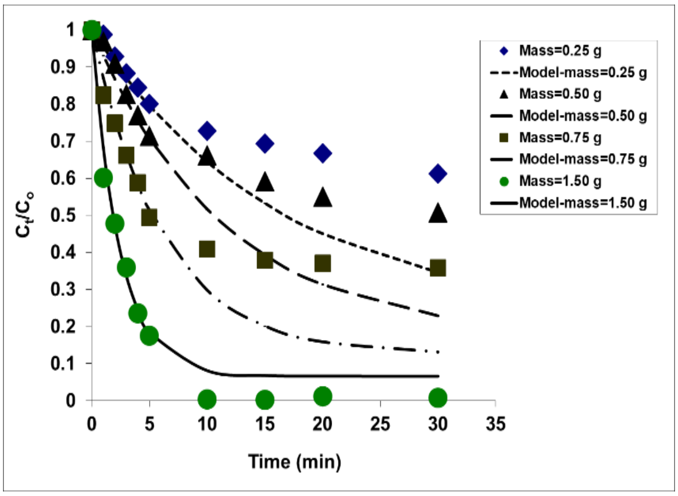

Fig. 4 Application of Furusawa-Smith model to the experimental data concentration 100 ppm, agitation 300 rpm, pH 7, size 500-710µm, volume 1.7 dm^3 and temperature 25°C.

experimental data in the initial period (first 5 minutes) after which a noticeable deviation is evident. Furthermore, the calculated q_e values are in great agreement with the experimental values during the first 5 minutes. This signifies that surface mass transfer was the controlling mechanism during the initial stage of the adsorption of MG, after which, the external mass transfer is no longer the predominant mechanism. Yakubu and Owabor (2018) reported that external film diffusion is the predominant mechanism during the initial period of the adsorption process.

2.4.2 Intraparticle Diffusion Model

Since the external mass transfer model failed to predict the kinetics data over the whole time interval, intraparticle mass transfer resistance is likely to be the rate-controlling step especially after the ending of the initial period of adsorption. Thus, the intraparticle diffusion model was employed to predict the experimental kinetics data. This model presumes the diffusion of adsorbate within the pore structure of the adsorbent. The expression of the intraparticle diffusion model is given in Eq. (3):

$$q_t = k_p t^{0.5} + c \tag{3}$$

where c (mg/g) is the intercept which is proportional to the boundary layer thickness; q_t is the adsorption capacity (mg/g) and k_p is the intraparticle diffusion rate constant (mg/ g. min$^{1/2}$). k_p can be obtained from the slope of the plot of q_t versus t$^{0.5}$.

Numerous previous studies have shown that the plot of q_t versus t$^{0.5}$ represents multi-linearity and attributed this to the fact that two or more steps may be involved in the adsorption process (Arivoli *et al*., 2009). **Figure 5** shows a plot of q_t versus t$^{0.5}$ for the adsorption of MG onto diatomite at a concentration of 50 ppm. It is evident from the figure the multiple nature of the relationship between q_t and t$^{0.5}$. The multi-linearity in the plot may suggest that the adsorption process of MG onto Jordanian diatomite is not fully controlled by intraparticle diffusion and the adsorption may be proceeded by surface adsorption followed by intraparticle diffusion. Lazaridis and Asouhidou (2003) attributed the last stages to the chemical reaction which supports the findings of the pseudo-second-order model. Yakubu and Owabor (2018) and Heydaria and Khavarpour (2018) announced that if the plot of q_t versus $t^{0.5}$ did not pass through the origin, this means that other steps may participate in the rate-controlling step. **Figure 5** shows that the linear portion of the curve does not pass through the origin and this indicates that intraparticle diffusion is not the only predominant mechanism for the adsorption of MG onto diatomite. Large values of "*c*" indicate the great contribution of surface adsorption in the rate-limiting step (Thilagavathi *et al.*, 2015). Sharma *et al*. (2016) reported that higher values of "*c*" indicate diffusion through the boundary layer is the rate-limiting step. Again, this supports the previous findings of the external mass transfer model as it was proved that the surface adsorption is predominant in the first five minutes. **Figure 6** shows an excellent fit of the intraparticle diffusion model to the experimental data for the adsorption of MG onto diatomite at different concentrations, and Table 3 records the results for the determination of intraparticle diffusion rate constant, k_p at different dosages of diatomite. Data from table 3 show that the value of k_p decreased from 23.86 to 7.153 (mg g^{-1}min$^{-0.5}$) as the diatomite mass increased from 0.25 to 1.5(g). As the mass of diatomite increased, a rapid decrease in MG concentration occurred and thus, reduces the driving force required for intraparticle diffusion.

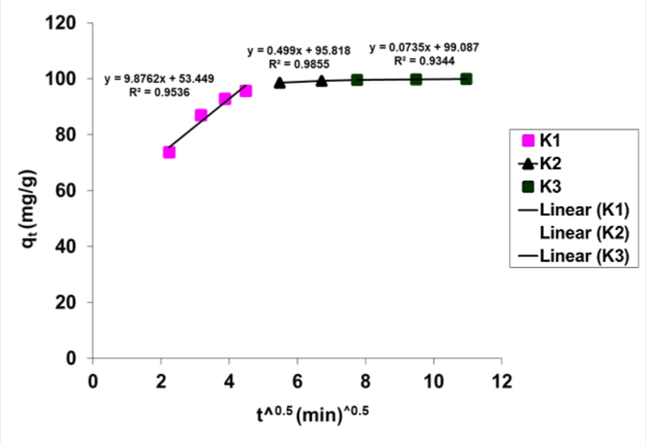

Fig. 5 Intraparticle diffusion effect on the adsorption of MG onto diatomite at concentration 50 ppm, agitation 300 rpm, mass 0.75 g, temperature 25ºC, pH 7, volume 1.7 dm^3 and size 500-710μm.

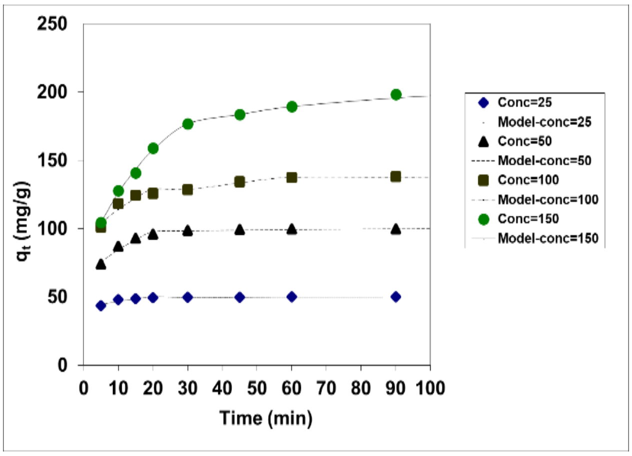

Fig. 6 Prediction of the intraparticle diffusion model to the experimental data. Temperature 25ºC, mass 0.75 g, agitation 300 rpm, pH 7, volume 1.7 dm^3 and size 500-710μm.

Table 3 Intraparticle diffusion rate constant, k_p, for the adsorption of MG onto diatomite as a function of the amount of diatomite.

Variable Mass (g)	k_{p1} (mg.g^{-1} min$^{-0.5}$)	c_1 (mg/g)	r^2	k_{p2} (mg.g^{-1}. min$^{-0.5}$)	c_2 (mg/g)	r^2	k_{p3} (mg.g^{-1}. min$^{-0.5}$)	c_3 (mg/g)	r^2
0. 25	23.860	29.050	0.9780	8.9230	106.90	0.9910	0.4320	172.30	0.7130
0.50	21.270	31.750	0.9870	1.0570	133.30	0.9280	2.4180	123.80	0.8710
0.75*	11.110	79.120	0.9000	3.9280	107.20	0.9760	0.2830	135.00	0.9250
1.50	7.1530	70.560	0.6560	0.0450	98.920	0.9130	0.0290	99.040	0.8730

** Standard experimental conditions, pH 7, agitation 300 rpm, particle size 500-710 µm, concentration 100 ppm, and mass 0.75 g.*

2.4.3 Pseudo Second-Order Kinetic Model

This model considers the adsorption process as a pseudo-chemical reaction process (chemisorption) and the overall adsorption rate is proportional to the square of the driving force. Ho and McKay (2000) expressed the kinetic rate equation in the linear form as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where k_2 is the rate constant of pseudo-second-order adsorption (mg/g.min), q_e is the equilibrium solid phase concentration (mg/g) and q_t is the solid phase concentration at time t (mg/g).

The Pseudo-second-order model was applied to the kinetics data in an attempt to determine the adsorption mechanism. Table 4 summarizes the pseudo-second-order rate constants for adsorption of MG onto diatomite. As seen from Table 4, there is good agreement between the values of the equilibrium adsorption capacity, $q_{e\ (Pred)}$, calculated by the pseudo-second-order model and the experimental values, $q_{e\ (Expt)}$. Moreover, the correlation coefficients, r^2, for the pseudo-second-order model are close to one (>0.99); this confirms the feasibility of the pseudo-second-order model to simulate the experimental data and implies that the adsorption mechanism of MG onto diatomite might be chemisorption (Chiou and Li, 2003). **Figure 7** further supports the pseudo-second-order model and shows the success of the model to simulate the experimental data for the adsorption of MG onto diatomite.

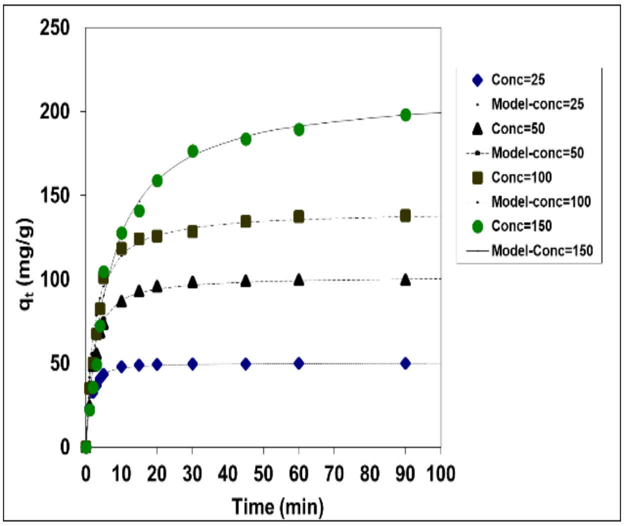

Fig. 7 Simulation of pseudo second-order model for the adsorption of MG onto diatomite. Temperature 25°C, agitation 300 rpm, size 500-710µm, mass 0.75, pH 7 and volume 1.7 dm^3. Concentration is in ppm.

Table 4 Pseudo second-order rate constants for the adsorption of MG onto diatomite.

Variable pH	K_2x10^3 (g/mg.min)	$q_{e(Pred)}$ (mg/g)	$q_{e(Expt)}$ (mg/g)	r^2	Conc. (ppm)	K_2x10^3 (g/mg.min)	$q_{e(Pred)}$ (mg/g)	$q_{e(Expt)}$ (mg/g)	r^2
5	1.440	131.42	129.81	0.9970	25	28.90	49.960	49.980	72.989
7*	3.018	138.10	138.09	0.9940	50	5.856	100.63	99.873	60.970
9	1.475	166.93	167.16	0.9950	150	0.696	201.42	198.58	31.540
11	2.202	200.36	198.54	0.9990	--------	---------	----------	---------	----------
Mass (g)									
0.25	0.457	183.28	176.76	0.9541					
0.50	0.947	150.39	149.38	0.9990					
1.500	12.04	99.337	99.350	0.9990					

* *Standard experimental conditions, pH 7, agitation 300 rpm, particle size 500-710µm, concentration 100 ppm, and mass 0.75 g.*

2.4.4 Transport Number

The transport number is usually utilized to investigate the mode of diffusion process (Yakubu and Owabor, 2018). The transport number can be expressed in a linearized form as in Eq. (5):

$$Log\frac{q_t}{q_e} = LogK_m + nLogt \tag{5}$$

Where K_m is the adsorbent-adsorbate interaction coefficient and n is the transport number.

The transport mechanism can be identified based on the value of n. According to Girish and Murty (2016), a value of n= 0.5 would suggest the Fickian mechanism (a surface mechanism), whereas a value of n=1 would indicate a non-Fickian mechanism. The values of K_m and n are summarized in Table 5 at different masses of diatomite. It is clear from Table 5 that the values of n are below 0.5 referring to the Fickian diffusion mechanism (surface diffusion) where MG interacts on the surface of diatomite. In surface diffusion, adsorbate particle migrates along the pore surface and hops from one adsorption site to another in a series of adsorption-desorption reactions (Hajjai *et al*., 2001).

Table 5 Constants of the Transport number model at different masses of diatomite

Mass(g)	**n**	**K_m**
0.25	0.275	0.329
0.50	0.208	0.429
0.75	0.079	0.717
1.5	0.003`	0.987

* *Standard experimental conditions, pH 7, agitation 300 rpm, particle size 500-710 μm, concentration 100 ppm, and temperature 25°C.*

2.4.5 Biot Number

Biot number is a useful tool applied to the kinetic data to analyze the rate-controlling step during the adsorption process. Biot number is a dimensionless group that relates the external mass transfer coefficient, k_f, to the intraparticle diffusion coefficient, D_e, and is given in Eq. (6) (Girish and Murty, 2016):

$$B_i = \frac{k_f d}{D_e} \tag{6}$$

Where d is the adsorbent's particle diameter (m); D_e is the intraparticle diffusion coefficient (m^2/min), and k_f is the external mass transfer coefficient (m/min). Intraparticle diffusion is the rate-controlling step if Biot number is greater than 100 and film diffusion is the expected rate-controlling step if Biot number is lower than 100. The intraparticle diffusion coefficients were calculated using Eq. (7) and Eq. (8) (Viegas *et al*., 2014):

$$Ln\left[1 - F(t)^2\right] = -\frac{\pi^2 D_e}{r^2} t \tag{7}$$

and

$$F(t) = \frac{q_t}{q_e} \tag{8}$$

Where r is the particle size radius assuming spherical geometry (m) and $F(t)$ is the fractional attainment of equilibrium. D_e values were calculated from the slope of the plot of Ln $[1\text{-}F(t)^2]$ versus t. All the calculated values were in the range of 10^{-9}. According to Vinod and Anirudhan (2001), the value of D_e in the rage of 10^{-6}-10^{-8} indicates that film diffusion is the rate-controlling step, while for pore diffusion, the value should be in the range of 10^{-11}-10^{-13}. Thus, the value of D_e in the range of 10^{-9} may refer to the fact that the adsorption process is not purely controlled by film diffusion and particle diffusion was involved in the later stages. This is in agreement with the earlier findings of Furusawa-Smith and intraparticle diffusion models. Both models confirm that neither film diffusion nor intraparticle diffusion is the sole rate-controlling step during the whole adsorption process. The calculated Biot numbers were larger than 100 for all the experimental conditions studied which is an indication of the predominance of the intraparticle diffusion. Despite Biot number results, one cannot exclude the effect of the external mass transfer process especially during the initial period of the adsorption process and the possibility of chemisorption as indicated by the results of the pseudo-second-order model.

2.4.6. Boyd Model

Boyd's model is considerably used to predict the actual rate-controlling step in the adsorption process. The model is expressed as follow (Viegas *et al*., 2014):

$$B_t = -Ln\frac{\pi^2}{6} - \ln(1-F(t)) \quad , \quad \text{for F(t) > 0.85} \qquad (9)$$

$$B_t = \left(\sqrt{\pi} - \sqrt{\pi - \frac{\pi^2 F(t)}{3}}\right)^2 \quad , \quad \text{for F(t) <0.85} \qquad (10)$$

According to this model, if the plot of B_t versus time is linear and passes through the origin, then intraparticle diffusion is the rate-controlling step. On the other hand, if the plot is nonlinear or linear but does not pass through the origin, then film diffusion or chemisorption is the rate-controlling step (Viegas *et al*., 2014). According to Viegas *et al*. (2014), Boyd's plots often have a multilinear nature. **Figure 8** displays the Boyd plot for the adsorption of MG onto Jordanian diatomite at two different concentrations. It is obvious from the figure the multilinear nature of the Boyd plot. Boyd plot reveals that the intraparticle diffusion mechanism is not the dominant mechanism and indicates the involvement of other mechanisms in the adsorption process of MG onto diatomites such as film diffusion and chemisorption.

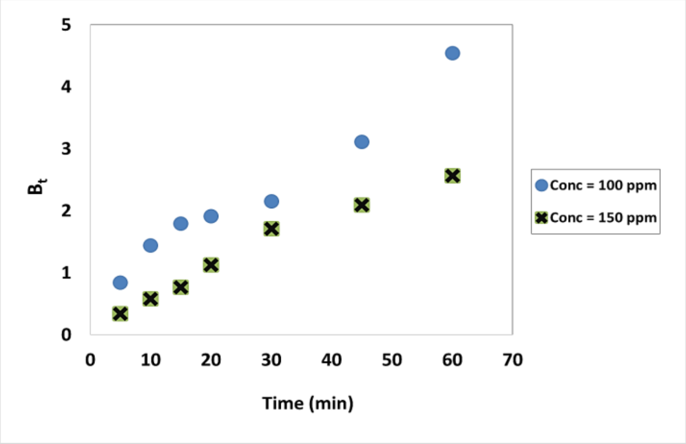

Fig. 8 Boyd plot for the adsorption of MG onto diatomite.

2.4.7 Elovich Model

Elovich model is usually applied to chemisorption systems in which the adsorbent is heterogeneous. The linear form of the Elovich equation is written as follow (Ramachandran *et al*., 2011):

$$q_t = \frac{1}{\beta} Ln(\alpha\beta) + \frac{1}{\beta} Lnt \qquad (11)$$

Where α is the initial rate of adsorption (mg/g.min) and β is the adsorption constant related to the extent of surface coverage and the activation energy for chemisorption (g/mg). **Figure 9** shows the goodness of fit of the Elovich model to the experimental data for the adsorption of MG onto Jordanian diatomite. It is clear from the figure that the model was able to simulate the kinetic data quite well and this supports the earlier findings of the equilibrium and kinetic studies. Equilibrium study showed that the experimental data are best presented by the Freundlich model and this confirms the heterogeneous nature of diatomite. Moreover, the kinetics study revealed that the adsorption mechanism might be chemisorption through the application of the pseudo-second-order model.

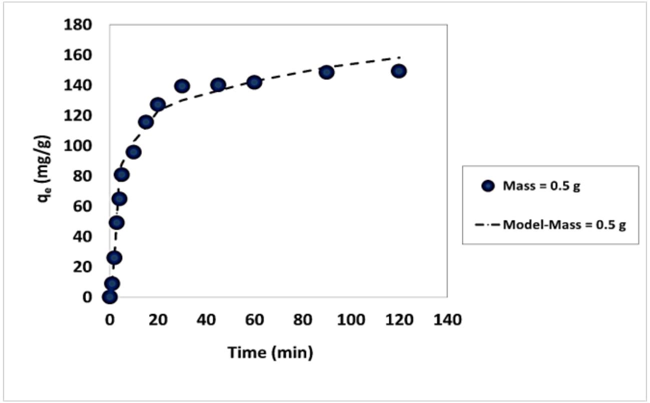

Fig. 9 Simulation of Elovich model for the adsorption of MG onto diatomite.

Conclusions

Adsorption kinetics that governs the removal of MG from aqueous solution was investigated under various conditions. The degree of removal of MG was found to be dependent on the experimental conditions. The higher amount of Jordanian diatomite showed a significant increase in the rate of MG adsorption with approximately 99% of dye removal. The kinetics performance of Jordanian diatomite was very well at the basic condition. The higher the initial MG concentration, the slower the rate of adsorption. Kinetics data were in good agreement with the pseudo-second-order kinetic model which confirms the chemisorption's nature of the adsorption process of MG onto Jordanian diatomite. The Elovich model was able to describe the adsorption process of MG and confirms the heterogeneous nature of Jordanian diatomite. The overall rate of the adsorption of MG onto Jordanian diatomite is controlled by film and intraparticle diffusion processes; during an initial period, the external mass transfer is the predominant mechanism followed by intraparticle diffusion with the possibility of chemisorption.

Nomenclature

C_o	=Initial dye concentration	[mg/ dm$^{3]}$
C_t	=Concentration of MG solution at time t,	[mg/ dm^3]
d	=Adsorbent's particle diameter	[m]
D_e	=Intraparticle diffusion coefficient	[m^2/in]
F(t)	=Fractional attainment of equilibrium	[-]
k_f	=External mass transfer coefficient	[m/min]
k_L	=Langmuir constant	[dm^3/g]
K_m	=Adsorbent-adsorbate interaction coefficient	[-]
k_p	=Intraparticle diffusion rate constant	[mg/g.min$^{1/2}$]
K_2	=Rate constant of pseudo second-order adsorption	[mg/g.min]
m	=Mass of the diatomite	[g]
m_v	=Coefficient of adsorbent	[g/dm^3]
n	=Transport number	[-]
q_e	=Equilibrium solid phase concentration	[mg/g]
q_t	=Amount of MG adsorbed at time t,	[mg/g]
r	=Particle size radius assuming spherical geometry	[m]
S_s	=Specific surface area	[m^{-1}]
t	=Time	[min]
V	=Volume of MG solution	[dm^3]
α	=Initial rate of adsorption	[mg/g.min]
β	=Adsorption constant related to the extent of surface coverage	[g/mg]

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Removal of Paracetamol from Wastewater by Calcined Gypsum: Adsorption and Kinetics Study

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It has been established that the presence of paracetamol in wastewaters can cause a potential risk to the environment. This work examined the possibility of using calcined gypsum in removing paracetamol from aqueous solutions. At neutral pH conditions, calcined gypsum was successful in removing paracetamol via adsorption, from aqueous solutions with a removal efficiency that ranged between 56.8 to 65.3 % of an initial concentration of 600 ppm. Increased temperature (from 20 to 50^0C) had a minor effect on the removal % of paracetamol while increasing the initial calcined gypsum dose (from 0.5 gm to 3 gm) and contact time (up to 15 min) increased by the removal % of paracetamol. Thermodynamically, the adsorption of paracetamol by calcined gypsum process was found to be spontaneous and endothermic, and more likely a physical process, while kinetically; the Pseudo-Second order model was found to be the best fit compared to the Elovich model. The removal process mainly consists of two stages, and it could be deduced from the kinetic behavior of paracetamol adsorption that the recrystallization process can be another rate-limiting step in the process.

Keywords: Paracetamol, Calcined Gypsum, Adsorption, Kinetics Study, Pseudo-Second Order.

Introduction

Paracetamol is one of the most important pollutants in industrial wastewater; although the amounts of paracetamol detected in different locations are usually low, however, the long-term discharge may cause potential risk to the environment (Kong *et al*, 2006). Paracetamol is a common analgesic and antipyretic drug (Kong *et al*, 2006), has widespread usage as the raw material of many drugs. Removal micro-pollutants including paracetamol from wastewater was achieved by; physical treatment (Ayyash *et al.*, 2015), biological methods and/adsorption followed by ultrafiltration/microfiltration separation(Ayyash *et al.*, 2015; Karaman *et al.*, 2016), chemical treatment(Kong *et al.*, 2006; Felis and Miksch, 2009), advanced oxidation process (Felis and Miksch, 2009; Ratpukdi, 2014), as well as membrane separation techniques (Ayyash *et al.*, 2015). Several authors have studied the treatment of micro-polluted in wastewater especially paracetamol using physio/chemical methods, such as adsorption There is a wide range of adsorption materials used for paracetamol removal, this includes activated carbon (Cabrita *et al.*, 2010; Ayyash *et al.*, 2015). Membrane separation technologies and adsorption are the most common methods in paracetamol removal from wastewater. Ayyash *et al.*, (2015) investigated the performance of membrane systems for wastewater treatment and paracetamol removal. Another attempt was done by Nadour et. al. (2019) regarding the removal of different compounds including paracetamol using a carbon-polymeric membrane. Terzyk, A. P. (2002), have studied paracetamol adsorption at neutral pH. Cabrita (2010), studied the removal of analgesic compounds using activated carbons from urban residues. While Beninati (2008), studied the adsorption of Paracetamol using commercial activated carbons, Villaescusa (2011) studied the paracetamol removal by vegetable wastes. El-Rimawi, *et al.*, (2018), studied the removal of Paracetamol as well as some selected pharmaceuticals micro-pollutants from aqueous solutions by using natural Jordanian Zeolite. While Velichkova (2017), studied heterogeneous Fenton oxidation for Paracetamol removal by the use of zeolite. Gypsum is mainly identified as a soft sulfate mineral that is composed of calcium sulfate Di-hydrate (Bello *et al.*, 2013; Cornelis and Cornelius, 1985). Gypsum was applied successfully and extensively for the removal of dye (Rauf et al, 2009), pharmaceutical drugs and heavy metals (Igwegbe *et al*, 2019). Gypsum represents a more advantageous, cheap, and readily available adsorbent due to its abundance in nature and it not requiring pretreatment as an adsorbent (Rauf *et al.*, 2009).

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A multitude of researchers successfully used calcined gypsum in wastewater treatment. Igwegbe *et al*, (2019) utilized it for the removal of Phenol. Al-Rawajfeh *et al*, (2018) successfully used calcined gypsum in the removal of Ibuprofen, while Al-Itawi (2019) utilized it for the removal of Fluoride from artificial wastewater.

Paracetamol was previously found to be a retarder of crystallization of calcium sulfate hemihydrate (Plaster of Paris) (Alrawashdeh et al, 2014). This interaction with paracetamol takes place in the water when calcium and sulfate ions crystallize forming calcium dehydrates, where paracetamol in the solution will adsorb and ultimately incorporate in the crystallization process. The purpose of this work is to study the ability to use gypsum as a low-cost material for the removal of Paracetamol from wastewater. In addition to identifying the effects of mass of adsorbent (gypsum), contact time and solution temperature on the removal of Paracetamol under neutral pH conditions. Finally, the thermodynamics and kinetics of the adsorption process were investigated.

1 Materials and Methods

1.1 Materials

The gypsum was produced from Jabal Mulaih, in Tafila, Southern part of Jordan (Alrawashdeh, *et al*, 2014), and it was supplied by Rawabi for Mining Co., a local mining company located near Tafila Technical University, it mainly consists of calcium sulfate dihydrate ($CaSO_4.2H_2O$), where it was crushed, milled and then calcined at 150-200^{0}C. Paracetamol (99%) was obtained from Al-Hikmah Co., Amman, Jordan. Paracetamol stocks were prepared by dissolving 100 mg of Paracetamol in 100 mL distilled water. This stock solution was then used in the preparation of synthetic wastewater samples with different concentrations.

1.2 Adsorption Assays

Batch sorption assays were conducted in a series of 500 mL glass beakers containing 250 mL of the Paracetamol solution. A predetermined amount of calcined gypsum depending on the assay was added to each one of the beakers. Experiments were conducted at an ambient temperature of 250C, and the desired temperature, with a stirring time of 5–25 minutes. Experiments were conducted at neutral pH because earlier studies show that paracetamol favors adsorption in natural pH (Ferreira *et al*, 2015; Bernal *et al*, 2017) After the completion of each assay, samples were filtered. The filtrate of Paracetamol solutions was then subjected to UV-visible analysis to determine the remaining concentration (SPECTRACOMP602; Advanced Products, Milan, Italy). A calibration curve of absorbance against different concentrations of Paracetamol was constructed. The samples of Paracetamol solutions had been analyzed by UV before and after treatment to determine the amount of Paracetamol removed.

1.3 Calculations

1.3.1 Paracetamol removal

Batch Paracetamol removal was evaluated by accounting for its initial and final concentrations. Assuming that the only removal mechanism is through adsorption, Paracetamol removal is evaluated as:

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

where C_o is the initial concentration of Paracetamol (mg/l) and C_e is the equilibrium Paracetamol concentration (mg/l). Gypsum adsorbed Paracetamol is calculated by:

$$Q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

where Q_e is the gypsum adsorbed Paracetamol concentration (mg/g), V the sample volume (L), and m is the used gypsum mass (g).

1.3.2 Adsorption Thermodynamics

The different thermodynamic parameters of the adsorption process will be evaluated through the effect of temperature on the thermodynamic equilibrium constant (K), which is defined as follows:

$$K = {}^{a_s}/_{a_e} = (v_s \times Q_e)/(v_e \times c_e) \tag{3}$$

whereas is the activity of the adsorbed ion, ae is the activity of the in-solution ion at equilibrium, v_s is the activity coefficient the adsorbed ion, and v_e is the activity coefficient of the in-solution ion at equilibrium. The activity coefficients can be assumed to equal unity, as the in-solution ions concentration approaches zero. Eq. 3 can be simplified to:

$$\lim(Q_{e\to 0}) \Rightarrow K = {}^{a_s}/_{a_e} = {}^{Q_e}/_{c_e} = {}^{c_o - c_e}/_{c_e} \tag{4}$$

The change in standard free energy of adsorption (ΔG^0) is calculated by:

$$\Delta G^0 = -R \times T \times \ln(K) \tag{5}$$

where R is the universal gas constant (8.314×10^{-3}kJ/K) and T is the temperature (K).

Change in Entropy (ΔS^0) and Enthalpy (ΔH^0) are evaluated through the Van't Hoff equation:

$$\ln(K) = \Delta S^0/R - \Delta H^0/RT \tag{6}$$

Values of ΔH^0 and ΔS0were obtained by fitting Equation 6 to values of *ln(K)* versus *1/T*.

1.3.3 Adsorption kinetics

Adsorption kinetics describes the uptake rate of Paracetamol, which can describe the residence time of ions at the solid-liquid interface. The kinetics of adsorption depends mainly on: the sorbent surface area and the nature-concentration of the active sites responsible for the interaction with the targeted ions (Yuh-Shan, 2004). Additionally, Adsorption kinetic models are used to study the probable rate governing step. The kinetics of the adsorption of Paracetamol on gypsum was studied using the pseudo-second-order, Elovich kinetic model, and Intra-particle diffusion model.
The pseudo-second-order kinetics can be represented as follows (Ho, 2006):

$$t/_{Q(t)} = 1/_{K_2} + t/_{Q_e} \tag{7}$$

where *t* is the contact time (min), *Q(t)* is the adsorbed Paracetamol at time t (mg/g), K_2 is the pseudo-second-order adsorption rate constant (g/mg.min). Values for the kinetic constant are evaluated by fitting dynamic adsorption data (*t/Q(t)* vs. *t*) to Eq. 7.
The Elovich kinetic model is expressed as (Abdelkreem, 2013; Riahi *et al*,, 2017):

$$Q(t) = ln(\alpha\beta)/\beta + \ln(t)/\beta \tag{8}$$

where α is the initial adsorption rate (mg/g min) and β is a parameter related to the extent of surface coverage and the activation energy for chemisorption (g/mg). Values for α and β are evaluated by fitting dynamic adsorption data (*Q(t)* vs. *t*) to Eq. 8.
The intra-particle diffusion equation can be written as (Reddy *et al*, 2012; Igwegbe *et al*, 2019):

$$Q(t) = k_{Pi} t^{1/2} + c_i \tag{9}$$

where C_i is a constant that provides an idea regarding the thickness of the boundary layer (mg/g) and k_{Pi} is the intra-particle diffusion rate constant (mg/g.min1/2). Values for ci and k_{Pi} are evaluated by fitting dynamic adsorption data (*Q(t)* vs. *t*) to Eq. 9.

2 Results and Discussion

2.1 Effect of temperature on Paracetamol removal

Figure 1 shows the Paracetamol removal percentage and the adsorbed amount by calcined gypsum at different operating temperatures. The influence of solution temperature on the removal of Paracetamol was investigated by varying the temperatures from 20 to 50^{0}C. As shown in Fig. 1, the adsorption of Paracetamol on gypsum increased slightly with increasing temperature, where it varied between 56.8% and 59.9% between 20 and 50^{0}C, respectively. Similarly, the amount of Paracetamol uptake by gypsum ranged between 34.1 and 35.9 (mg/g) between 20 and

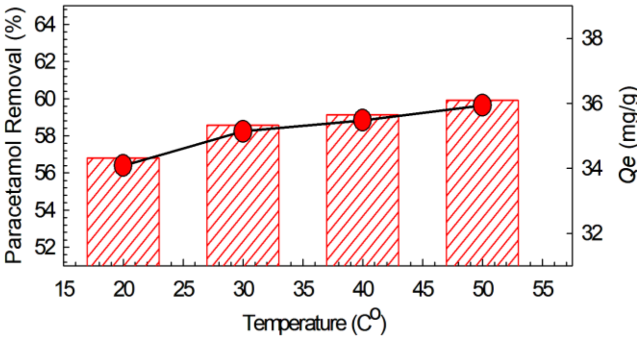

Fig .1 Paracetamol removal percentage and adsorbed amount at various temperatures after 5 min and with 1 gm of gypsum.

50^{0}C, respectively. These results indicate that at the conditions of this experiment, the increased temperature did not have any effect on the amount of Paracetamol removed by gypsum.

2.2 Effect of gypsum dose on Paracetamol removal

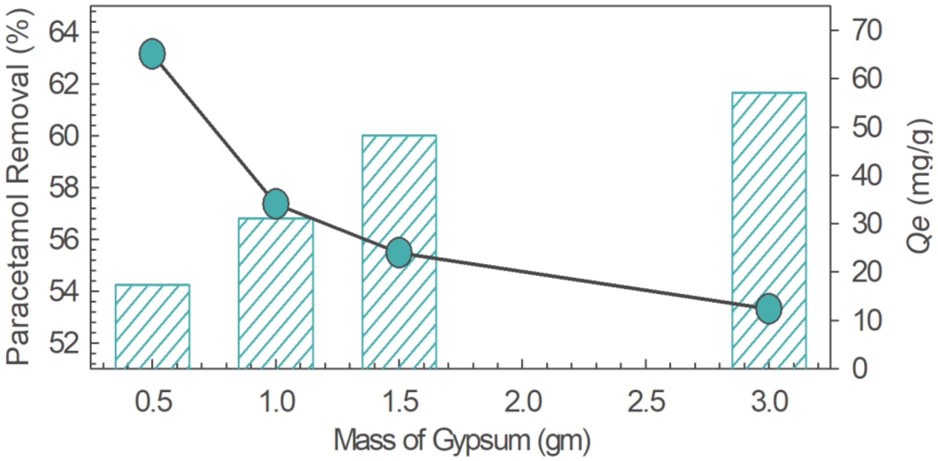

Fig. 2 Paracetamol removal percentage at different initial gypsum dose after 5 min at 20^{0}C.

Figure 2 shows the Paracetamol removal percentage and adsorbed amount by calcined gypsum at different initial doses. Mass of gypsum was increased from 0.5 to 3 g, the percentage of Paracetamol removed on the adsorbent (gypsum) increased from 54.2% to 61.6 %. The increase in Paracetamol removal with increasing mass of gypsum is as a result of the increase in the number of adsorption sites and adsorbent surface area. The amount of Paracetamol per unit mass of the gypsum (Q_e) decreased with increasing adsorbent loading from 65.1 to 12.3 (mg/g). This is due to not fully using the adsorption cites at a higher adsorbent loading (Radnia *et al*, 2012; Gorzin and Abadi, 2018). A smaller dose of adsorbent will be saturated more quickly than a larger one (Meniai, 2012).

2.3 Effect of contact time on Paracetamol removal

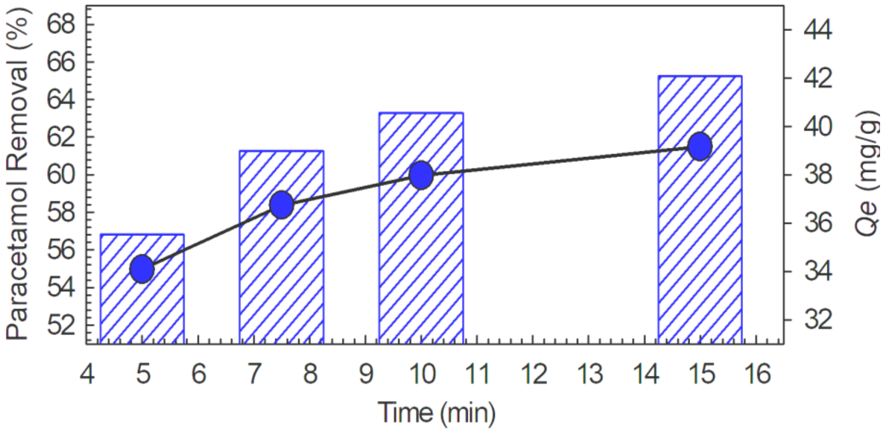

Fig. 3 Paracetamol removal percentage at different contact times with 1 gm of gypsum at 20^{0}C.

Figure 3 shows Paracetamol removal percentage and adsorbed amount by calcined gypsum at different contact times with 1 gm of gypsum at 20^{0}C. As seen in the figure, the maximum Paracetamol removal was obtained at the highest contact time studied (15 min). The removal rate ranged varied between 56.8% and 65.3% between 5 and 15 min, respectively. This can be explained by the fact that the frequency of collision of the adsorbing material increasing with retention time, which increased the process of adsorption (Ahmadi and Igwegbe, 2018; Benosmane *et al*,, 2018). Also, the adsorption sites were more available with time, resulting in the amount of Paracetamol per unit mass of the gypsum (Q_e) increasing from 34.8 to 39.2 (mg/g).

2.4 Adsorption thermodynamics

Table 1 shows the different thermodynamic parameters for the adsorption process, and **Figure 4** shows the Van't Hoves plot for the system, and Figure 4 shows the Van't Hoff plot for the adsorption of Paracetamol on calcined gypsum.

Table 1 Thermodynamic properties for the adsorption of Paracetamol on calcined gypsum

Temperature (°C)	K *(mol/L)*	ΔG^0 *(J/mol)*	ΔH^0 *(J/mol)*	ΔS^0 *(J/mol/K)*
20	1.315	-678.4	3218.3± 542.3	13.3± 1.8
30	1.414	-857.9		
40	1.447	-915.9		
50	1.494	-994.8		

As seen in Table 2, the negative value of ΔG^0 indicates the spontaneous nature of the adsorption of paracetamol on gypsum. However, values of ΔG^0 were found to be relatively small; less than 1 kJ and varied slightly at increasing temperatures. ΔG^0 for physical adsorption is between -20 and 0 kJ/mol (Babakhouya *et al*, 2010; Atkins *et al*, 2018), implying that the adsorption of Paracetamol on gypsum is a physical adsorption process. Positive value of ΔH^0 indicates the Paracetamol adsorption process is endothermic (Babakhouya *et al*, 2010; Adeogun and Balakrishnan, 2017), while the positive ΔS^0 the value obtained indicate that the increase in the degree of disorderliness of the adsorbed species (AlOthman *et al*, 2014) and the affinity of the gypsum adsorbent for Paracetamol. This explains the lowered removal percentage calculated at higher temperatures. Moreover, due to a negative ΔS_0, the process of adsorption will increase disorder and randomness

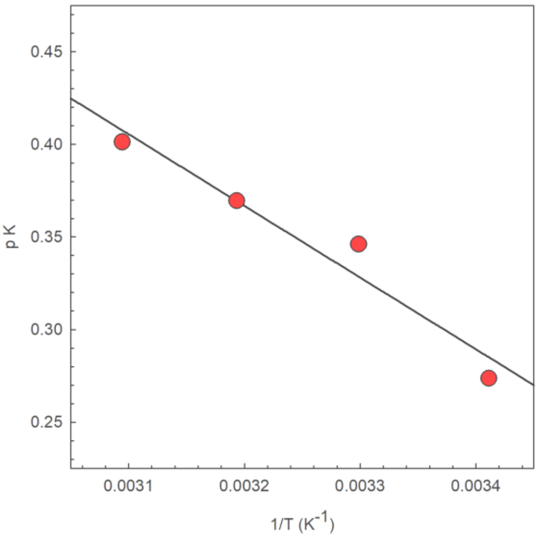

Fig 4. Van't Hoff plot for the adsorption of Paracetamol on calcined gypsum. Straight line represents Eq. 8 in the form: $pK = \Delta S/8.314 - (\Delta H/T)/8.314$ with an R2 value of 0.946**.**

2.5 Adsorption kinetics

Table 3 shows the kinetic parameters for the pseudo-second-order and the Elovich kinetic model fitted to the dynamic adsorption data. **Figures 5A** and **5B** show the kinetic Paracetamol adsorption data fitted to the pseudo-second-order kinetic model and the Elovich model

Table 3 Parameters for the pseudo-second-order and the Elovich kinetic models; values are presented as the best estimate ± standard error.

Model	Pseudo-Second order	Elovich
Parameters	K_2 = 36.61±2.06 (g/mg.min) Qe = 42.22±0.27 (mg/g)	α = 1666.3±167.6 (mg/g.min) β = 0.218±0.031 (g/mg)
R^2	0.9967	0.961

Considering the values given in Table 2 for the regression coefficient, it is clear that with an R^2 value of 0.9967 that the adsorption kinetic data obeys the pseudo-second-order model well. In contrast, the values of R^2 for the Elovich model was 0.961, indicating that the pseudo-second-order model better represents the adsorption behavior. This behavior of calcined gypsum, when used as adsorbent, was reported by Igwegbe and colleagues (Igwegbe et al, 2019) in the adsorption of Phenol.

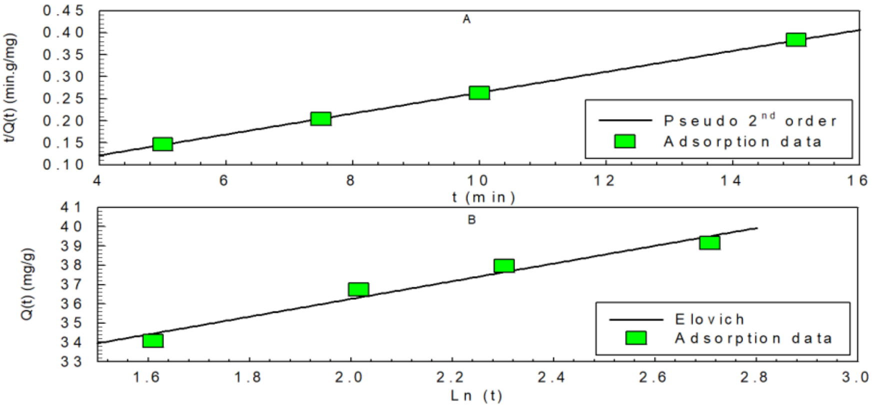

Fig 5. Kinetic Paracetamol adsorption data fitted to pseudo-second order kinetic model, and the Elovich model; lines represent the fitted model and points represent the data.

Table 4 Parameters for the Intra-Particle Diffusion kinetic model, as single and two stages; values are presented as best estimate ± standard error.

Intra-particle Diffusion	Single Stage	Two Stages	
Parameters	k_{Pi}= 3.01±0.62(mg/g $min^{0.5}$) c_i =27.95±1.91 (mg/g)	*Stage 1* k_{Pi}= 4.234±0.68 (mg/g $min^{0.5}$) c_i = 24.78±1.87 (mg/g)	*Stage 2* k_{Pi}= 2.076±0.33 (mg/g $min^{0.5}$) c_i = 31.18±1.08 (mg/g)
R^2	0.921	0.975	0.976

For the Intra-Particle Diffusion Model Table 4 shows the kinetic parameters for the dynamic adsorption data fitted to the model as a single-stage and a two-stage process.

Figures 6A and **6B** show the kinetic parameters for both scenarios. Fitting the data to a single-stage process resulted in a lower R^2 value (0.921) compared to a two-stage process (0.975 and 0.976). This indicates that indeed the removal of paracetamol by calcined gypsum is a two-stage process. The first stage in the intra-particle diffusion model can be attributed to instantaneous adsorption onto the outer surface, while the second stage represents gradual adsorption taking place where the adsorbate travels within the pores of the adsorbent (Hameed et al, 2008). As seen in Table 4, the initial instant adsorption stage had a higher k_{Pi} (4.234±0.68 vs. 2.076±0.33 (mg/g $min^{0.5}$)), and a lower c_i (24.78±1.87 vs. 31.18±1.08 (mg/g)), indicating a faster rate and a smaller thickness of the boundary layer in the first stage.

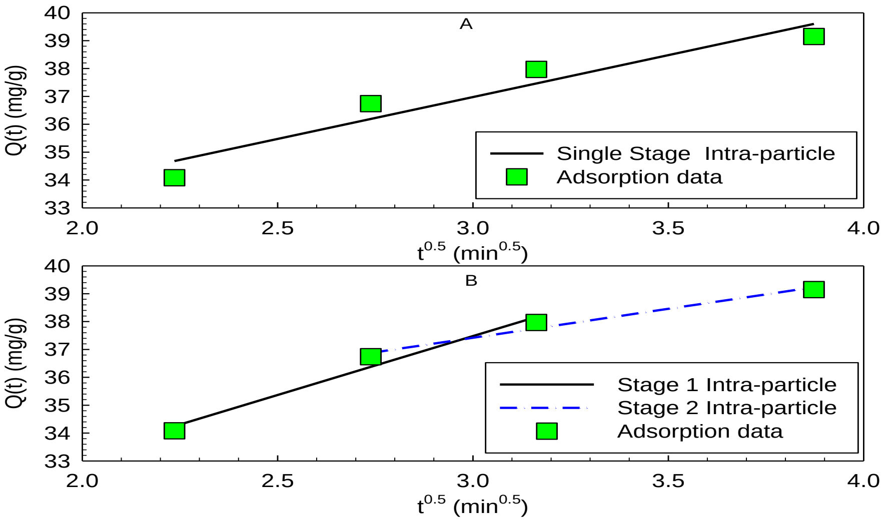

Fig. 6 Kinetic Paracetamol adsorption data fitted to the Intra-Particle Diffusion model as a single and two stages; lines represent the fitted model and points represent the data.

One final observation could be made after examining Figure 6, in the intra-particle diffusion model plot, the line between the data points did not pass through the origin point, which may indicate that the intra-particle diffusion is not the only rate-limiting step in paracetamol adsorption (Ma *et al*, 2013). This additional step can be attributed to nature by which paracetamol interacts with calcined gypsum (i.e. inclusion in the re-crystallization process) (Alrawashdeh et al, 2014).

Conclusions

The potential and ability of calcined gypsum in removing paracetamol from aqueous solutions were investigated. Effects of calcined gypsum mass, contact time and solution temperature on the adsorption process were studied. Calcined gypsum was found to be able to remove paracetamol, via adsorption, from aqueous solutions at neutral pH conditions. The increased temperature had a minor effect on the removal of paracetamol while increasing the initial calcined gypsum dose and contact time increased the removal of paracetamol.

The adsorption process was found to be spontaneous and endothermic, evident by the thermodynamic parameters, and more likely is a physical adsorption process. Kinetically, the adsorption of paracetamol by calcined gypsum was found to be best represented by the Pseudo-Second order model, followed by the Elovich kinetic model. Finally, the Intra-particle diffusion model analysis indicated that the removal process mainly consists of two stages. Also, it could be deduced from the kinetic behavior of paracetamol adsorption that the recrystallization process can be another rate-limiting step in the process.

Nomenclature

Symbols

C_0	=Initial concentration of paracetamol	[mg/l]
C_e	=Equilibrium concentration of paracetamol	[mg/l]
C_i	=Constant in the intra-particle diffusion equation model	[mg/g]
t	=Time	[min]
Q_e	=Gypsum adsorbed concentration of paracetamol	[mg/g]
$Q_{(t)}$	=Gypsum adsorbed concentration of paracetamol at time t	[mg/g]
V	=Sample volume	[l]
m	=Gypsum mass	[g]
K	=Thermodynamic equilibrium constant	[mo/l]
K_2	=Pseudo second order adsorption rate	[g/mg.min]
k_{pi}	=Rate constant in the intra-particle diffusion equation model	[g/mg.min1/2]
a_s	=activity of the adsorbed ion	[-]
a_e	=activity of the in-solution ion at equilibrium	[-]
v_s	=activity coefficient of the adsorbed ion	[-]
v_e	=activity coefficient of the in-solution ion at equilibrium	[-]
R	=The universal gas constant	[kJ/K]
T	=The temperature	[K]
ΔG_0	=Change in standard free energy	[J/mol]
ΔH_0	=Change in enthalpy	[J/mol]
ΔS_0	=Change in ntropy	[J/mol.K]

Greek letters

α	=First parameter in the Elovich kinetic mode	[mg/g.min]
β	=Second parameter in the Elovich kinetic mode	[g/mg]

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Hydrologic System Protection by Decentralized Wastewater Treatment Technologies in Jordan

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The nine different technologies are constructed at the pilot scale in one experimental site at Al-Balqa Applied University and use the same wastewater characteristics as the inlet. Monthly samples were collected from the inlet and outlet of nine different decentralized wastewater treatment technologies for three years (June 2016-June 2019). The samples were analyzed for physical, chemical, and biological parameters including TSS, Turbidity, pH, COD, DO, NH_4, NO_3, TN, BOD, and *E. coli*. Removal efficiencies for the nine technologies are obtained for COD, BOD, TN, and TSS to be above 95%. NH_4 the removal efficiencies for the nine technologies vary and found to be in the range of 27 to 76% while for the *E. coli* in the range of 65 to 95%. Further, data on energy consumption were collected for each technology and found for the nine investigated technologies in the range of 0.03 to 0.30 Jordan Dinars per treated cubic meter. The investigated technologies were evaluated, and the best options were endorsed. It is concluded that the adaptation of decentralized wastewater treatment will certainly help protect the hydrologic system in Jordan especially in the high lands where significant groundwater recharge occurs and a considerable amount of surface water flows towards Jordan Valley and collection dams.

Keywords: Wastewater, decentralized wastewater treatment, contamination, pollution, innovative technologies, removal efficiency.

Introduction

Jordan depends mainly on groundwater for domestic uses and blended reclaimed water with surface water for irrigation (Fach *et al*, 2010). Major cities are served with centralized wastewater collection systems but this is not the case in rural areas. Establishing and operating collection and treatment systems in rural areas are not economically feasible because the users are highly scattered and the topography is significantly variable (Brunner *et al.*, 2018). The situation is further complicated because most of Jordan's renewable groundwater resources are located in the high lands, mostly on top of limestone aquifers. These aquifers are vulnerable to groundwater contamination by cesspits (Burde *et al.*, 2001). Lately, the government of Jordan is dedicating part of their attention and budget to promote decentralized wastewater treatment as an option for groundwater protection and therefore sustainable hydrologic system (Hussein, 2019).

Decentralized wastewater systems are considered for communities up to 5000 inhabitants (Nanninga *et al.*, 2012). For more than this number, centralized wastewater collection and treatment systems are more suitable (Massoud *et al.*, 2008). To be specific, decentralized wastewater systems are suitable for communities in remote areas, hotels, industries, and households in rural areas (Chong *et al.*, 2012). Another important aspect of decentralized wastewater treatment is the reuse part (MWI 2016). Due to the water shortage, it is very useful for residents and farmers to have access to reclaimed water that can be used for supplementary irrigation. However, what is the type of technology end-users should adopt and what cost, and whether it is safe and sustainable (Khattiyavong *et al.*, 2019). Based on these facts, this research is performed to partially answer these questions and to provide feasible clarifications that may help academia, managers, and end-users form an adequate decision based on a scientific approach.

Non-conventional water resources can be used for food production systems after proper treatment for the rehabilitation of marginal and degraded lands in the Middle East and North Africa (Hussain *et al.*, 2019). Different wastewater technologies are commercially used for the treatment of municipal as well as industrial wastewater (MWI, 2016).

Wetland technologies, SBR, septic tank, modified septic tank, and biofilm systems are successfully implemented in Jordan in one of the important demonstration research centers and in several cities in Jordan (Wang *et al.*, 2019). Furthermore, it is necessary to ensure the local water quality required, a cost-effective treatment, sustainability, and protection of public health. The development and adaptation of these technologies and solutions have considered the local conditions and climate change (MWI, 2019).

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The general classification of decentralized wastewater treatment systems includes the following (Singh *et al.*, 2014):

- Natural treatment systems

Aerobic systems: Suspended growth, attached growth, and Combined suspended and attached growth. Anaerobic systems: Suspended growth, Attached growth. Combined (aerobic/anaerobic/natural) systems. Anaerobic–aerobic, Anaerobic–natural, and Anaerobic–aerobic–natural

Following is a brief description of the investigated technologies constructed at the research facility at Al-Balqa Applied University during this research:

- Septic Tanks and Modified Sept Tanks Systems

The system is based on a modification of the conventional septic tank by including an integrated aerated-settling chamber. Two modules of bacterial growth (suspended and attached) are tested to treat domestic wastewater (Abbasi *et al.*, 2018). Unlike the suspended growth reactor, the anaerobic/aerobic fixed bed reactor contains corrugated plastic sheets, where the microorganisms are attached to the surface of the packing material (Ambica and Raman, 2015).

- Sequencing Batch Reactor (SBR) Systems, SBR is a discontinuously operated fill- and draw-activated sludge process. The unit consists of a clear water pump, aerator and de-sludging pump (Beuna *et al.*, 1999). All the reactors are operated in the mode with feed, anaerobic, aerobic, settling and decanting phases and therefore all biological, oxidation, sedimentation, nitrification, and de-nitrification processes occur in a single tank. On the other hand, a continuous batch reactor designed to reduce electrical consumption. Two settling tanks designed in a way to separate the suspended solids from the treated water. Aeration, de-sludging, and feeding are done by a small compressor.

a. Wetland Systems: Multi-stage Single-pass Vertical Filter system that was designed to produce high-quality effluent passively. The system consists of a septic tank (primary treatment), first stage vertical filter (secondary treatment and nitrification), organic denitrification reactor (removal of nitrate), and a second stage vertical filter (pathogen reduction and further polishing) (Vymazal, 2005).

b. A recirculating vertical filter system that is consists of a septic tank for primary treatment, followed by a recirculation tank. Effluent is pumped from the recirculation tank onto the vertical filter before then flowing through a flow splitting device from where a portion of the effluent is returned to the recirculation tank while the rest leaves the system and is used for irrigation. The system is designed to treat 2 m³/day (Vymazal, 2010) and (Masia and Martinuzzi, 2007).

- French Systems

The French version of vertical-flow constructed wetlands is characterized by treating directly raw wastewater on a first-stage filter (Prost-Boucle and Molle, 2015). The advantage of the French system is that it takes raw sewage directly to its first stage and treats the primary sludge on the surface of the first stage beds. This greatly facilitates sludge management as compared to systems which need to deal with primary sludge (Esser *et al.*, 2014).

1Materials and Methods

1.1 Experiment Design

The experiments were designed to critically analyze and discuss data and results obtained from experimental methods to assess the microbial population dynamics in wastewater treatment technologies, and to evaluate the process performance and characteristics of physical, chemical, and biological wastewater treatment processes. This research is carried out in the above-mentioned research facility at Al-Balqa Applied University. Samples were collected on the same day and time each month, and the analysis was carried out in the laboratory which is prepared with all necessary equipment and test kits. The data is examined, validated, and finally approved before its stored and used for analysis. Some tests were occasionally re-taken to ensure data reliability and accuracy. The technologies monitored were selected to be all the available technologies in the facility, the inlet, and outlet sampling points were the same for the entire period of sampling to ensure consistency.

The design parameters were selected to cover all concerns and to answer all possible research questions Domestic raw water in the research facility is unlikely to have heavy metals or pharmaceutical residuals. However, one test was made at the beginning of the sampling period to confirm this fact. The samples were analyzed for physical, chemical, and biological parameters including Total Suspended Solids (TSS), Turbidity, Potential Hydrogen (pH), Chemical Oxygen Demand (COD), Dissolved Oxygen (DO), Ammonium (NH_4), Nitrate (NO_3), Total Nitrogen (TN), Biological Oxygen Demand (BOD), and *Escherichia coli* (*E. Coli*) all in mg per liter. Further, data on energy consumption were collected for each technology. As mentioned above, the experiments carried out over three years on nine different decentralized wastewater technologies installed in the research facility. The systems dimensions are standards for the nine technologies with 3 meters long, 2 meters width and 1.5 meters depth. The flow rate is calibrated to be 2 cubic meters per 24 hours and controlled with the control panel.

1.2 Analysis

The main objective of this research is highly connected to the identification of the most efficient technology considering technical and economical constraints. Hence, it is important to compare the analysis across the different technologies, with proper interpretations and reasonable conclusions. It is worth mentioning that the effluent not only controlled by the process itself but with external conditions such as climatic conditions and raw wastewater characteristics (Almanaseer *et al* , 2012). Hence, it is important to consider these facts when trying to establish trends and variability among the different variables. The correlation was considered, graphical representation as well. More elaboration on this and pictorial representations are presented in the result section.

2 Results and discussion

Table 1 shows a summary of the average monthly values for the different parameters throughout this research (June 2016–June 2019). Significant variations in effluent water quality are observed among different technologies. However, all the technologies fulfill the required standards for reclaimed water reuse. Also, **Figure 1** shows graphical representations of the performance for the nine different technologies. The performance is calculated based on eight parameters relative to the water quality of the raw water before and after treatment. All parameters are found below the reuse standard. But, there is noticeable variability among the different technologies in terms of their performance. This is normal since different technologies operate different principals and advanced processes and influenced differently by local conditions such as raw wastewater characteristics and climatic variations. Table 2 shows the average, minimum, maximum, and standard deviation of the monthly data for the nine examined technologies

Table 1 Long-term average values for the different technologies

Technology	COD	BOD	TN	NH_4	NO_3	TSS	DO	pH	Turbidity
Septic Tank	54.0	16.2	65.3	14.1	1.2	20.3	2.8	7.3	13.2
Modified Septic Tank	69.9	18.6	63.1	45.5	1.4	32.5	2.9	7.5	11.7
Sequencing Batch Reactor with Ultraviolet (SBR-UV)	61.4	15.8	93.0	30.4	6.8	32.5	3.2	7.5	12.8
Sequencing Batch Reactor with Ultraviolet manufactured by PUROO Company (SBR-PUROO)	46.8	16.8	46.1	26.7	1.7	24.8	3.3	7.6	12.0
Vertical Wetland (V-Wetland)	25.0	10.0	105.2	0.9	65.2	19.2	5.0	7.6	2.5
Recirculated Wetland (R-Wetland)	106.0	21.5	84.6	9.8	47.6	34.3	3.2	7.3	19.3
Aerated Wetland	20.7	11.0	46.6	0.6	36.6	18.0	7.0	8.0	3.5
Second wetland	34.1	16.3	33.3	4.1	27.1	16.6	4.6	8.0	2.8
French aerated wetland	15.8	8.3	30.1	0.9	25.1	16.6	7.4	8.3	1.5
Raw wastewater	863.0	612.3	128.4	69.7	0.7	805.5	0.6	7.1	331.2

On the other hand, the removal efficiency as a percentage showed slight variations among the different technologies but overall the removal efficiency is high and promising. For TN, the removal efficiency is less but this is suitable for reuse where reclaimed water is rich with nitrogen to compensate for fertilizers necessary for plant growth. Removal for DO, pH, and Turbidity is not considered since the focus is on the biochemical parameters. The energy consumption varies where wetland technologies consume less energy in comparison to the septic tank and SBR technologies and the removal efficiency of the nine technologies (Table3).

Table 2 Minimum, maximum, and standard deviation of the monthly data for the nine technologies

Technology	Statistics	COD	BOD	TN	NH_4	NO_3	TSS	E-coli	DO	pH	Turbidity
Septic Tank	Average	54.0	16.2	65.3	14.1	1.2	20.3	94354	2.8	7.3	13.2
	STD	4.7	2.6	10.0	7.4	1.3	4.7	23273	0.7	0.8	4.0
	Max	60.8	22.0	81.3	29.4	4.7	30.0	158500	4.7	7.7	22.1
	Min	44.3	12.0	50.8	4.8	0.3	14.0	67600	2.0	4.7	8.2
Modified Septic Tank	Average	69.9	18.6	63.1	45.5	1.4	32.5	70685	2.9	7.5	11.7
	STD	9.2	2.8	6.8	9.5	1.4	8.2	24674	0.6	0.1	3.7
	Max	86.9	25.0	72.0	63.1	5.2	44.0	133400	3.7	7.7	16.4
	Min	54.6	14.0	50.2	28.6	0.3	12.0	43100	2.0	7.2	4.3
SBR-UV	Average	61.4	15.8	93.0	30.4	6.8	32.5	547	3.2	7.5	12.8
	STD	13.2	5.8	20.2	7.9	3.5	9.7	115	0.7	0.2	9.9
	Max	77.7	29.0	138.6	39.4	13.2	50.0	805	5.3	7.9	44.2
	Min	27.2	10.0	51.3	8.6	2.2	16.0	359	2.1	7.1	4.4
SBR-PUROO	Average	100	30	45	0.0	30	50	100	2	9	10
	STD	500	200	70	0.0	45	200	1000	0.0	9	0.0
	Max	150	60	70	0.0	80	60	1000	1	9	0.0
	Min	50	15	45	5	30	50	2	2	9	2
V-Wetland	Average	25.0	10.0	105.2	0.9	65.2	19.2	569	5.0	7.6	2.5
	STD	3.8	2.9	19.0	0.6	18.6	3.6	68	1.0	0.2	1.3
	Max	34.6	15.0	132.8	2.0	101.2	26.0	670	6.5	7.8	6.2
	Min	20.4	6.0	61.1	0.2	42.6	14.0	471	3.5	7.3	1.2
R-Wetland	Average	106.0	21.5	84.6	9.8	47.6	34.3	285962	3.2	7.3	19.3
	STD	20.8	2.6	15.2	10.1	12.5	5.4	76874	0.6	0.2	5.2
	Max	140.0	25.0	127.6	33.4	69.2	44.0	435200	4.0	7.6	25.6
	Min	55.4	16.0	68.6	2.6	31.6	28.0	160200	2.5	7.0	12.3
Aerated Wetland	Average	20.7	11.0	46.6	0.6	36.6	18.0	600	7.0	8.0	3.5
	STD	6.7	2.3	2.4	0.3	4.2	13.4	58	0.9	0.1	1.7
	Max	35.0	15.0	49.6	1.1	44.8	50.0	693	7.9	8.1	6.3
	Min	13.3	8.0	42.6	0.0	31.2	8.0	512	5.2	7.7	1.3
Second wetland	Average	34.1	16.3	33.3	4.1	27.1	16.6	4796	4.6	8.0	2.8
	STD	3.0	1.2	2.1	1.2	2.0	4.6	409	0.4	0.0	0.3
	Max	38.4	18.0	37.5	6.2	30.4	24.0	5580	5.2	8.1	3.1
	Min	28.0	14.0	30.4	2.8	24.4	10.0	4360	4.0	7.9	2.1
French aerated wetland	Average	15.8	8.3	30.1	0.9	25.1	16.6	327	7.4	8.3	1.5
	STD	5.8	2.0	1.7	0.5	4.3	4.6	54	0.6	0.3	0.2
	Max	25.6	12.0	32.9	1.9	31.4	24.0	402	8.0	8.7	1.8
	Min	10.0	6.0	27.7	0.2	18.4	10.0	259	6.2	7.9	1.2

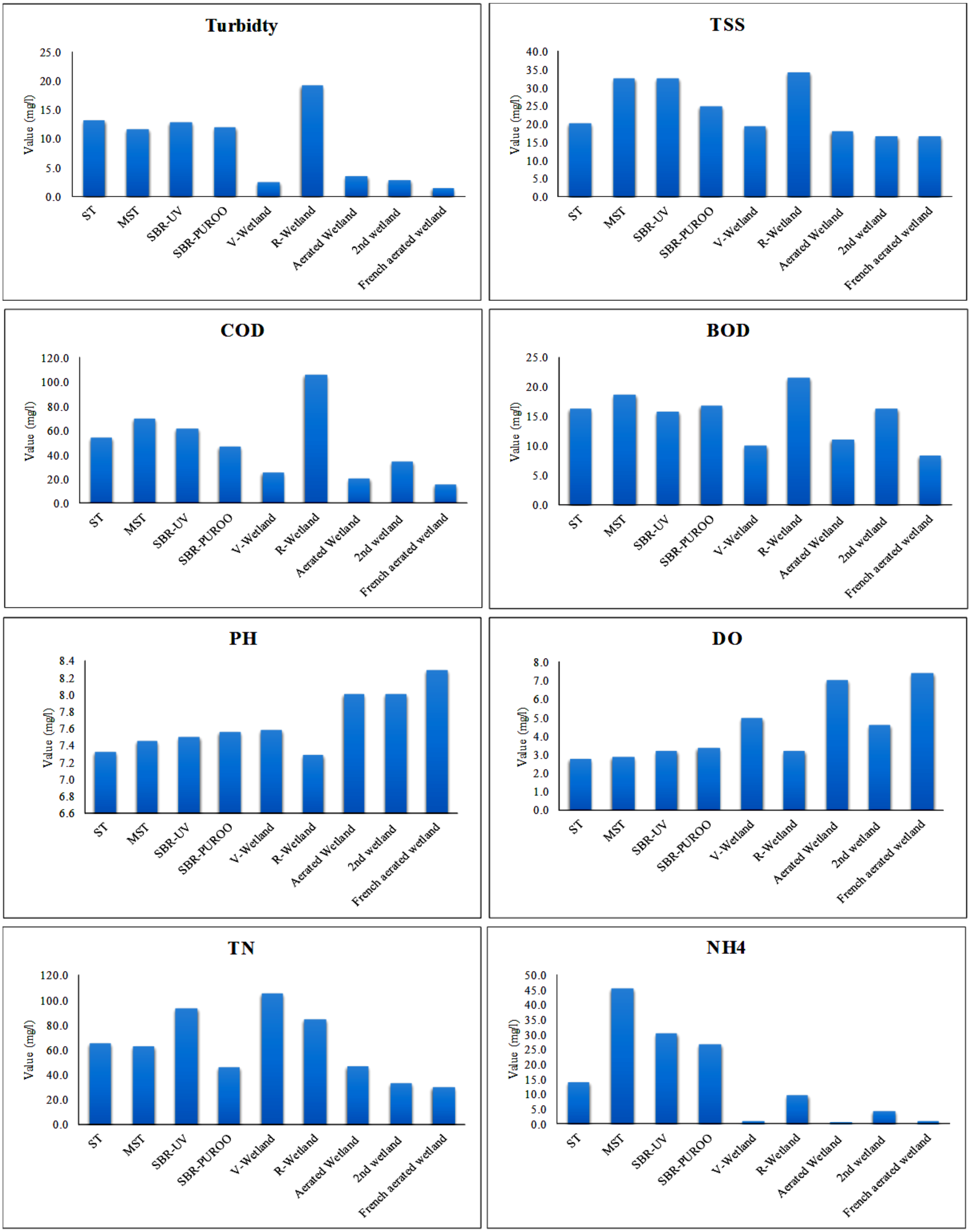

Fig. 1 Performance of different technologies

Table 3 Removal efficiency (%) and energy consumption (Jordan Dinar, JD)

Technology	COD	BOD	TN	NH4	*E. Coli*	TSS	Energy consumption (JD*/m^3)
Septic Tank	94.1	97.4	99.5	49.14	79.4	97.47	0.30
Modified Septic Tank	91.1	95.96	99.6	50.9	73.4	95.97	0.30
SBR-UV	92.8	96.4	99.9	27.6	65.54	95.97	0.23
SBR-PUROO	94.5	97.3	99.9	64.11	80.86	96.93	0.25
V-Wetland	97.7	98.8	99.9	38.1	68.72	97.6	0.05
R-Wetland	92.7	96.5	99.6	34.14	75.72	95.74	0.08
Aerated Wetland	97.5	99.03	99.9	63.75	89.18	98.79	0.03
2nd wetland	96.5	98.6	99.9	74.1	94.03	98.89	0.03
French aerated wetland	98.1	99.3	99.9	76.55	92.6	99.44	0.04

1 (Jordanian Dinar, JD)= 1.4097 USD

The removal efficiency follows the same trend for the different parameters but with different magnitudes. For example, *E-Coli* has the highest removal efficiency which is promising followed by TSS which is very important since the water re-use normally practiced using dripping irrigation. Lessor no TSS helps in avoiding pipes clogging. Overall, this similarity in removal pattern for all the parameters indicates consistency in the treatment processes for the nine technologies and therefore, more selection criteria are necessary to choose the best option. Energy consumption is one possible selection criterion. Finally, and concerning the treated wastewater standards, the efficiency of each technology was calculated as the percentage of removal. This indicator reflects the ability of each technology to remove the loads and hence to purify the wastewater. The effluent was compared to standards category A, B, and C to ensure the reliability of treated wastewater but also as a measure of efficiency. Table 4 shows the treated wastewater standards.

Table 4 Treated wastewater reuse standards

Standards	COD	BOD	TN	NH4	NO$_3$	TSS	*E. coli*	DO	pH	Turbidity
Irrigation-Class A	100.0	30.0	45.0	N/A	30.0	50.0	100	2.0	9.0	10.0
Irrigation-Class B	500.0	200.0	70.0	N/A	45.0	200.0	1000	N/A	9.0	N/A
Water discharge	150.0	60.0	70.0	N/A	80.0	60.0	1000	1.0	9.0	N/A
Artificial recharge	50.0	15.0	45.0	5.0	30.0	50.0	2	2.0	9.0	2.0

Figure 2 shows a pictorial representation of the possible relationship between COD and BOD for the nine investigated technologies. Although the points are only nine and not enough to establish strong statistical significance, still we can have an idea about the possible correlation between COD and BOD. These significant correlations indicate that the processes are working successfully and the collected samples and analysis are valid. COD tends to follow COD in wastewater treatment processes. On the other hand, TN is significantly correlated with NH4 indicating efficient nitrogen removal. However, a good amount of nitrogen remains in the treated wastewater which is good for re-use. Overall, this high level of removal ensures hydrologic system protection, both when we discharge the treated wastewater to rivers, or when we use for irrigation. The quality of the treated wastewater is suitable for groundwater recharge (Hubbard *et al.*, 2016). However, this statement needs more analysis and not within the scope of this paper.

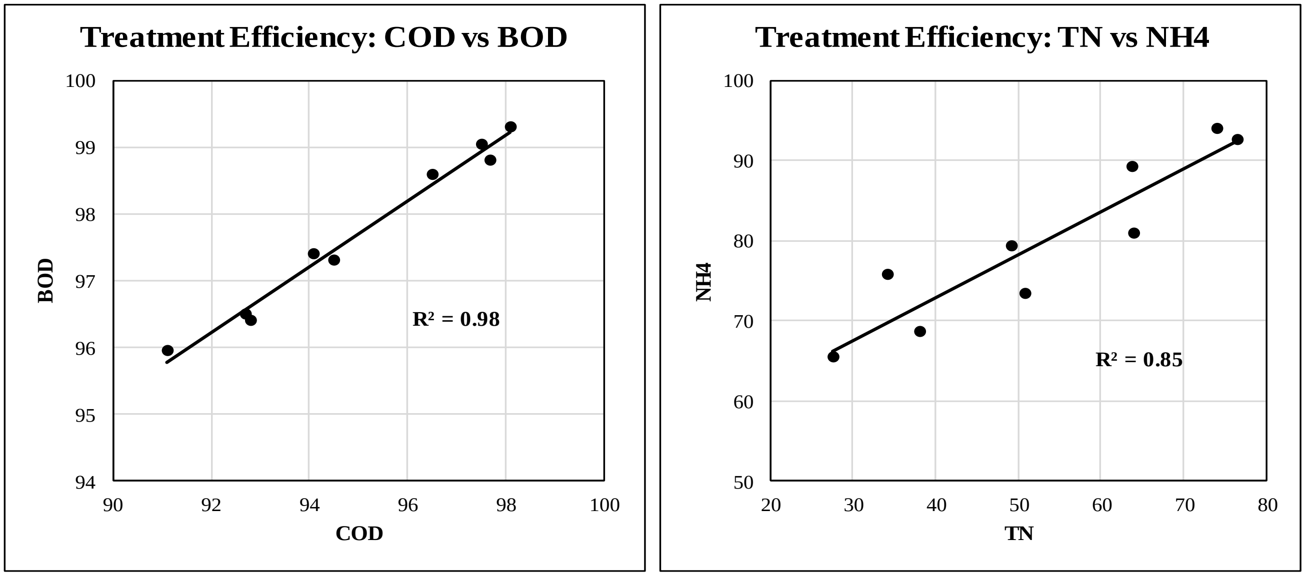

Fig. 2 Treatment efficiency (%) for COD vs BOD (left) and TN vs NH_4 (right) for nine technologies

Conclusions

Adopting decentralized wastewater treatment options has great potential for protecting soil and water resources from contamination. Cesspits continue to pollute water resources in Jordan, especially in rural areas, and hence an integrated water resources plan should include decentralized wastewater as one of its alternative strategies to consider wastewater as an opportunity rather than a challenge. Most of the renewable groundwater resources in Jordan are distributed within karst limestone aquifers which are highly vulnerable to contamination by raw wastewater. The collection and on-site treatment of raw water will certainly alleviate the potential contamination of soil and groundwater. As an output of this research, the results show clearly that the investigated technologies perform well for organic matter removal and nitrification and make sludge management easy. Following are five lessons learned:

1- Three years of continuous monthly data is considered a decent amount of data to examine the performance of decentralized wastewater treatment technologies. The collected monthly data over three years allowed us to derive solid conclusions and reliable results. However, it is difficult to compare the technologies concerning their costs because it depends on the local economic conditions.
2- Centralized wastewater options are not feasible in rural areas where communities are scattered. Hence, adopting decentralized wastewater treatment options will certainly protect the hydrologic system; surface water and groundwater, and will provide treated wastewater for supplementary irrigation and therefore alleviate the stress on domestic water resources.
3- The collected data is proven consistent and reliable, and hence we can build solid conclusions and decisions on the analysis, especially for the comparison between the different technologies in terms of their performance. Wetland technologies seem to be more feasibly subject to the availability of space.
4- The energy consumption varies from 0.04 to 0.30 JD per cubic meter of treated wastewater. This is not the only cost item, operation and maintenance require additional cost too. Overall, the cost varies across different technologies but the wetland system is more economically feasible.
5- Treatment was very efficient in terms of E-Coli and TSS which are the most important parameters. Also, technologies show consistency in their performance which makes the decision on the best technology easier. The excellent removal of E-Coli ensures health protection and the removal of TSS ensures efficient irrigation systems with less maintenance.

Finally, if we consider the German experience, nearly 1.5 million decentralized wastewater treatment units are installed in rural areas, mainly to protect the hydrologic system. In Jordan, there are approximately 240 units mostly operating in houses, farms, hotels, and police offices in remote areas. This is a humble number and cannot help protect our hydrologic and environmental systems. This research shows the successful efficiency of the various technologies under Jordanian conditions using a scientific approach based on observations rather than estimations or simulations. The future in Jordanian rural areas is certainly for decentralized wastewater treatment technologies, and this is proven as a successful approach to protecting the hydrologic system.

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Nomenclature

Acronyms

AS	=Activated Sludge	[-]
BOD	=Biochemical Oxygen Demand	[-]
COD	=Chemical Oxygen Demand	[-]
CSTR	=Continuous stirred-tank reactor	[-]
E	=Effluent	[-]
OF	=Overflow	[-]
PD	=Pre-Denitrification	[-]
S	=Dissolved material concentration	[mg COD/l]
SE	=particulates separation coefficient	[-]
Si	=Dissolved material concentration in the feed	[mg COD/l]
SI	=Soluble inert organics concentration	[mg COD/l]
TKN	=Total Kjeldahl Nitrogen	[-]
UF	=Underflow	[-]
W	=Waste	[-]

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