

Adsorptive removal of some carbonyl containing compounds from aqueous solutions using Iraqi porcelanite rocks: a kinetic-model study

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ABSTRACT

The kinetics of removal of Acetaldehyde (A.Al), Benzaldehyde (B.al), 2-Butanone (2-But), Acetophenone (A.Ph) and Benzophenone (B.Ph) from their aqueous solution by adsorption onto powder of Iraqi Porcelanite rocks was investigated. The results were treated by non-linear pseudo-first order (PFO) and non-linear pseudo-second order (PSO) models, the latter model was better fitting with experimental data. Furthermore, the non-linear treatment indicates that the time periods of the operation is longer than that estimated from direct observation, hence the quantity of adsorption at equilibrium will be greater than observed directly. Another advantage of non-linear treatment not mentioned before is deducing kinetic model best fitting with data by expecting the equilibrium time of the process depending on the data points of initial time period. The obtained kinetic parameters were correlated with some molar parameters using multi-variable linear regression which show that molar polarizability has a promotional effect upon kinetic adsorption parameters, while molar volume and hydrophobicity have a demotion effect. The kinetic investigation was extended to include diffusion Boyd', and Weber-Morris models. The results showed that A.Al and 2-But had a film diffusion kinetic determining step, the remaining compounds show a non-diffusional (local adhering) like behavior.

Keywords: Kinetics, Adsorption, Carbonyl compounds, Porcelanite.

Article type: Research Article.

INTRODUCTION

The carbonyl-containing compounds are typical volatile organic compounds and ubiquitously present in the environment (Yao *et al.* 2017). Low molecular weight carbonyl-containing compounds, such as formaldehyde and acetaldehyde, were classified by Richardson *et al.* as toxic and carcinogenic (Richardson, *et al.* 2007). They have further classified acetaldehyde among the compounds that have toxic properties of human carcinogens. Acetaldehyde was recognized as a compound that constitutes a great potential health risk (Hebert, *et al.* 2010). Acetaldehyde may take an important role in enabling the digestion and absorption of organic carbon and their incorporation into body tissues leading to undesirable bioactivity (Rice *et al.* 2012). The presence of aldehydes in surface waters could be a consequence of pollutants removal process from the atmosphere. Dąbrowska and Nawrocki have reported the observation of formaldehyde and acetaldehyde in water samples collected from precipitations and from surface water (Dąbrowska & Nawrocki 2013). Aldehydes are formed in drinking water during water disinfection processes as disinfection by-products (DBPs) upon the use of disinfectants such as ozone, chlorine, chloramines or chlorine dioxide. These disinfectants react with organic matter that are naturally occurring in water producing DBPs (Richardson, *et al.* 2007). A significant increase in the concentration of carbonyl compounds in treated water was observed as the time of reaction of Cl₂ and ClO₂ with aldehyde precursors increased (Dąbrowska *et al.* 2005). The unintentional health hazards caused by the formation of aldehydes during drinking water treatment processes, upon the use of disinfectants, could be minimized by the removal of the formed hazardous compounds. Several techniques have been employed for the removal of

pollutants from aqueous media during the past years. The commune techniques include filtration, precipitation, coagulation, distillation, adsorption and ion exchange resins (Sharma and Bhattacharya 2017). Adsorption was considered to be more advantageous in comparison with other techniques in that it consumes less energy, relatively simpler in operation (de Andrade *et al.* 2018) and of high efficiency in removing organic pollutants from wastewaters (Carmalin & Eder 2018). Adsorption was applied by Babić *et al.* for the recovery of aldehyde from aqueous streams using extractant impregnated resins as adsorbent (Babić van der Ham & de Haan 2006). Adsorption on activated carbon and on activated carbon and silica was used to reduce the concentration of acetaldehyde, among other aldehydes, from the malt-based agricultural distillate (Balcerak *et al.* 2017). The utilization of adsorbents other than activated carbon, which is the most common pollutants adsorbent, reflects the tendency of adsorption studies towards the use of an efficient and low-cost adsorbents (Gupta *et al.* 2009; Sharma & Bhattacharya 2017). This trend led to a growing interest in adsorbent material that are of natural bases. (Vidal & Moraes 2019). In that respect, several natural-based materials were reported to be used for removal of organic based pollutants from aqueous media. They include activated clays (Nayak & Singh 2007), porous clay heterostructure (Arellano-Cárdenas *et al.* 2005) Iraqi bauxite and surfactant-modified Iraqi bauxite (Al-Kazragi *et al.* 2017), bauxite clay (Kuang *et al.* 2020) and porcelanite (siliceous) rocks (Abu-Hawwas *et al.* 2020). The work presents a study on kinetics of removal of some carbonyl containing compounds by adsorption on Iraqi porcelanite rocks.

MATERIALS AND METHODS

Chemicals

The chemicals included in this study were Acetaldehyde (A.Al) and Benzaldehyde (B.Al) from BDH, 2-Butanone (2-But), Acetophenone (A.ph) and Benzophenone (B.ph) from Hannover. All were of high grade purity; A.Al and 2-But were further purified by normal distillation; B.Al and B.ph by vacuum distillation; B.ph by vacuum sublimation. Deionized water was used as a solvent.

Preparation of adsorbate

A Sample of porcelanite was obtained from Traifawi mine by General Company for Geological Survey and Mining, Iraq. The rocky form sample was grounded into powder, washed with deionized water to be free from dirt and water-soluble substances, dried in an oven at 80 °C for a period of 24 h, after getting cold, grounded again and sieved using sieve of ostensible size of $\leq 150\mu\text{m}$. The porcelanite powder was preserved in glass container that is sealable tightly. The analysis of porcelanite rocks revealed their chemical composition which is presented in Table 1. The oxides form was measured by X-ray fluorescence spectroscopy. Humidity content of the sample was measured by combustion method.

Table 1. The chemical analysis of porcelanite.

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	LOI
W (%)	74.03	3.65	0.98	5.63	5.66	0.01	0.18	0.07	9.70

Preparation of adsorbent solutions

The carbonyl compounds used in this work were dissolved in deionized water to prepare 100 ppm stock solutions, from which a series of solutions were prepared by dilution to perform the Beer-Lambert calibration curve for each compound at its λ_{max} with double beam Shimadzu 1800 spectrophotometer.

Conducting the experiments

A series of 12 flasks each one contains 20 mL of 30 ppm solution of the carbonyl compound, were placed in a shaking water bath seated at 25 °C. Shaking was hold after 30 minutes, then a 0.1 g of the adsorbent was added to each flask. Shaking was resumed and the zero time was recorded. In an intervals of 25 minutes, the flasks were taken out of the water bath one by one for analysis, the content of each flask was centrifuged and decant. The absorbance of each solution was measured at the desired λ_{max} . From these measurements the concentrations were computed using the Beer-Lambert calibration curve, and then the quantity of the adsorption was calculated from the following relation:

$$Q(t) = [C_o - C(t)] * \frac{V}{m} \dots \dots \dots (1)$$

where $Q(t)$ is the amount of carbonyl compound adsorbed per unit mass of adsorbate (mg/g) at time (t), C_o and $C(t)$ are initial solution concentration and the solution concentration at time (t) respectively given in mg/L or ppm units, V volume of the solution in L and m is the mass of the adsorbate in gram.

RESULTS AND DISCUSSION

The kinetic results of carbonyl compounds adsorption process on the surface of porcelanite rocks are shown in Table 2 where $Q(t)$ and Q_e (quantity of the adsorbed substance at equilibrium) are given in mg/g and mmole/g. Using mmole/g would give more realistic comparison of the adsorbed quantity of different adsorbents on the surface of porcelanite rocks. Initial observation indicates that at equilibrium, the adsorbed amount of the various adsorbent follows the order shown below.

$$A.ph > B - Al > A. Al > 2 - But > B.ph$$

The obtained results indicates that a period of 275-300 min was sufficient to complete the adsorption process. The obtained kinetic data were treated by a non-linear pseudo-first order PFO, as well as non-linear pseudo-second order PSO models, which are represented by equations (2) and (3) respectively :

$$Q(t) = Q_e [1 - e^{-k_1 t}] \dots \dots \dots (2)$$

$$Q(t) = \frac{Q_e^2 \cdot k_2 \cdot t}{1 + Q_e \cdot k_2 \cdot t} \dots \dots \dots (3)$$

The advantages of using nonlinear methods in treating data were discussed by many researchers such as Kajjumba et al. (2018), Kumar (2006) and Hameed & El-Khaiary (2008). However, non-linear models for kinetic data modeling were utilized in the present work to avoid the arbitrary estimation of the process constants, especially Q_e , where in these two models the values of Q_e were calculated numerically. These values can then be adopted in the more detailed kinetic treatments based on the diffusion model. The obtained adsorption kinetics data are presented in Figs. 1 and 2 for PFO and PSO models respectively. Table 3 lists the values of Q_e , rate constants and the values of the standard deviation, σ . Q_e values were adopted as a statistical criterion for the suitability of the nonlinear models to be applied to adsorption data.

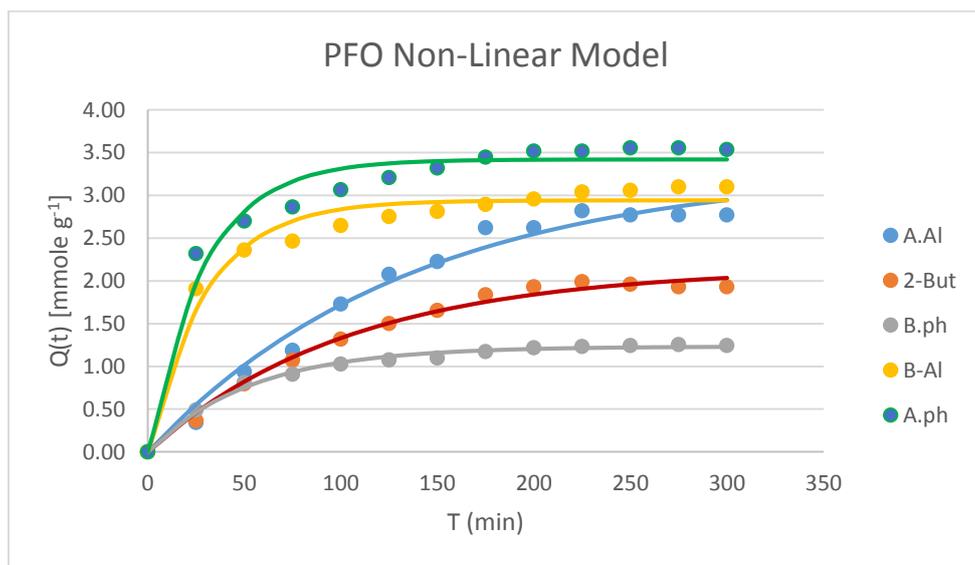


Fig. 1. Experimental data for adsorption kinetics are illustrated by discrete points and the continuous line shows the nonlinear PFO or Lagergren kinetic model adopted to process the results.

Table 2. Experimental data of the adsorption process in units of mg/g and mg/mole.

	A.Al	2-But	B.ph	B.Al	A.ph
t[min]	Q(t)[mg/g]	Q(t)[mg/g]	Q(t)[mg/g]	Q(t)[mg/g]	Q(t)[mg/g]
0	0.00	0	0	0	0
25	15.24	26.12	89.25	202.44	278.62
50	41.36	56.60	148.02	250.33	324.33
75	52.24	76.19	165.43	261.21	343.93
100	76.19	93.60	187.20	280.80	367.87
125	91.42	106.66	195.91	291.68	385.28
150	97.95	117.54	200.26	298.21	398.34
175	115.37	130.60	213.32	306.92	413.58
200	115.37	137.13	222.03	313.45	422.29
225	124.07	141.49	224.20	322.16	422.29
250	121.90	139.31	226.38	324.33	426.64
275	121.90	137.13	228.56	328.69	426.64
300	121.90	137.13	226.38	328.69	424.47
	A.Al	2-But	B.ph	B.Al	A.ph
t[min]	Q(t)[mmole/g]	Q(t)[mmole/g]	Q(t)[mmole/g]	Q(t)[mmole/g]	Q(t)[mmole/g]
0	0.00	0.00	0.00	0.00	0.00
25	0.35	0.37	0.49	1.91	2.32
50	0.94	0.80	0.81	2.36	2.70
75	1.19	1.07	0.91	2.46	2.87
100	1.73	1.32	1.03	2.65	3.07
125	2.08	1.50	1.08	2.75	3.21
150	2.23	1.66	1.10	2.81	3.32
175	2.62	1.84	1.17	2.90	3.45
200	2.62	1.93	1.22	2.96	3.52
225	2.82	1.99	1.23	3.04	3.52
250	2.77	1.96	1.24	3.06	3.56
275	2.77	1.93	1.26	3.10	3.56
300	2.77	1.93	1.24	3.10	3.54

Table 3. values of the kinetic constants obtained for the adsorption process through nonlinear treatment.

	A.Al	2-But	B.ph	B.Al	A.ph
k₁[min⁻¹]	0.007	0.010	0.019	0.033	0.034
k₂[mmole g⁻¹ min⁻¹]	2.542E-05	3.894E-05	8.525E-05	1.470E-04	1.207E-04
PFO Q_e [mmole g⁻¹]	3.32	2.16	1.23	2.94	3.42
PSO Q_e [mmole g⁻¹]	4.55	2.82	1.10	1.89	1.67
PFO σ [mmole g⁻¹]	0.14	0.07	0.03	0.15	0.19
PSO σ [mmole g⁻¹]	0.17	0.09	0.02	0.06	0.09

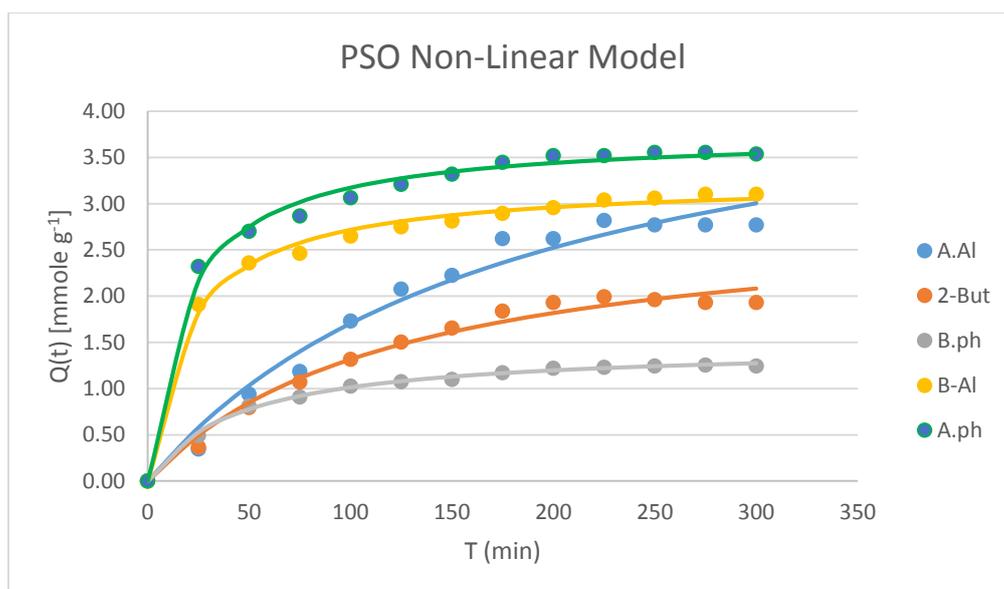


Fig. 2. The adsorption kinetics empirical data are illustrated by the discrete dots and the continuous line shows the nonlinear PSO kinetics model adopted to process the results.

In comparison with the previously presented one, the order of the adsorbed amount at equilibrium, Q_e of carbonyl compounds has changed remarkably when applying nonlinear PFO model:

$A.ph > A.Al > B-Al > 2-But > B.ph$ for PFO

Applying nonlinear PSO model gave more dramatic change:

$A.Al > A.ph > B-Al > 2-But > B.ph$ for PSO

The change of Q_e values order requires extending the adsorption process to longer periods of time up to 600 min according to non-linear PFO model, while it needs much longer periods according to PSO model. This result may be considered as additional advantage of non-linear regression, that in many situations the slight change of material concentration after a certain period of time makes it possible to record a wrong equilibrium time of the process, especially if that error lay within a systematic error of the experiment. Thus, with this information it is possible to estimate more accurate equilibrium time and hence equilibrium concentrations from a set of data points that did not reach Q_t . Furthermore, it is possible now to deduce more accurately the type of mechanism obeyed by the system under study; not only from the data before equilibrium but also from estimated equilibrium time that the system must have. This benefit of non-linear methods was not reported previously in the literature cited. While the initial observation of adsorbents Q_e increasing order showed that monocyclic aromatic carbonyl compounds i.e. A.ph and B-Al, were of highest Q_e , followed by the aliphatic carbonyl compounds i.e. A.Al and 2-But, and finally the bicyclic aromatic B.ph compound. Using the non-linear PFO and PSO kinetic models suggests the extension of the adsorption process over a longer period of time during which A.Al reaches the second place in the order of Q_e according to the PFO model and to the first place according to the PSO model. Cited literatures have shown strong tendency to model adsorption parameters with Quantitative Structure-Activity Relationship (QSAR) methods taking the advantage of the recent development in the information technology in both software and hardware fields (Pir et al. 2018; Brasquet et al. 1999; Roy et al. 2019; Ling et al. 2019). Therefore, in order to draw a comparison between the adsorption behavior of the studied carbonyl molecules, a set of molecular properties which are considered to have a direct contribution to the adsorption process were calculated. These properties included molar volume, logarithm of octanol /water distribution coefficient $\log P$ and the molar polarizability. These parameters were chosen for the following reasons:

- 1- Molar volume (V_m) would assist investigating the tendency of the studied molecules to penetrate inside the pores of Porcelanite rocks powder.
- 2- $\log P$ would be indicative of the contribution of the hydrophilic-hydrophobic factor of the substance to the adsorption process.

- 3- Molar polarizability (P) can be utilized as a measure of the attraction forces between the adsorbent molecule and adsorbate surface through dipole-dipole, dipole-induced dipole and even hydrogen bonding.

Table 4 shows the values of these parameters for the molecules under study. A multivariate linear regression model was adopted to study the dependence of each Q_e values and the rate constants on the above molar parameters as an independent variables (Table 5). It is clear that the PSO kinetic constants are more suitable for the assumed multi-linear model of the molecular parameters affecting the adsorption process.

Table 4. Calculated molecular assembly properties of adsorbent molecules.

	Mwt [g mole ⁻¹]	V _m [cm ³ mol ⁻¹]	logP	P [cm ³ mol ⁻¹]
A.Al	44	219.85	-0.580	4.53
2-But	71	327.11	1.010	8.20
B.ph	182	580.32	3.270	22.01
B-Al	106	385.00	1.720	12.36
A.ph	120	432.94	1.360	14.19

Table 5. Values of coefficients of molecular aggregate traits as independent variables within the multivariate linear regression model for the dependent kinetic variables in addition to the correlation coefficient.

	PFO Q _e	PSO Q _e	k1	k2
(Constant)	2.727	7.098	2.179E-02	1.801E-04
V _m	-0.001	-0.020	-8.364E-05	-8.123E-07
logP	-0.976	-0.417	-4.720E-04	2.814E-05
P	0.121	0.301	2.561E-03	1.479E-05
R (correlation coefficient)	0.769	0.950	0.536	0.566

In both kinetic models, the effect of increasing molar volume had a slight inverse effect on Q_e and on the rate constants of the adsorption process. This effect can be explained in the light of the decrease of the diffusion ability of the adsorbate within the adsorbent by increasing molar volume.

The low value of the inverse molar volume contribution coefficients reflects the nature of the average size distribution of the pores of the adsorbent material, which is either have a geometric diameter much larger than the diameter of the adsorbate particles or it has a small average distribution. So that the effect of surface porosity on the adsorption process was not large, however, it was clearly contributed to the increase in the value of Q_e for small molecules such as A.Al and 2-But. The value of the inverse volume contribution coefficient for PSO model is 20 times bigger than that of the PFO model, which is due to the fact that the PFO model is basically built on the basis that the activity of the adsorbate material dissolved in the solution is the main motivator of the adsorption process ignoring the surface contributions which include the porosity factor. The hydrophobicity factor of the adsorbate represented by $\log P$ contributes in a negative way to the outcome of the adsorption process in both models reflecting the repulsion between the hydrophobic adsorbate and the hydrophilic adsorbent surface. The value of the inverse proportion of the hydrophobic factor in the PFO model exceeds twice the corresponding value for the PSO model. The effect of this factor on the rate of the process differs completely in the two models, while it has an inverse proportional effect on the rate in PFO process, in the PSO model case its effect is direct proportional. This difference may be attributed to the fact that when the surface activity is taken into consideration along with the activity of the adsorbate in the PSO model, the initial deposition of organic hydrophobic matter on the hydrophilic surface of Porcelanite rocks powder works to shield the hydrophilicity locally, creating hydrophobic centers on the surface that act as nuclei that accelerate the adsorption process by reducing the activation energy barrier required for the process.

The polarization factor was found to be the major affecting factor with the largest contribution to the increase in the yield and rate of the adsorption process in both PFO and PSO models, this effect reflects the increase of the adsorbent /adsorbate bonding strength through the basic attraction forces.

Treatment of kinetic data according to the diffusion model

The Q_e values obtained from the non-linear treatment of PFO and PSO models were used to calculate the value of fractional uptake $F = Q(t)/Q_e$ to investigate the kinetics of the process from the perspective of the diffusion mechanism, in particular surface diffusion (film diffusion) and porous diffusion (intra-particle diffusion). Boyd's equation for surface diffusion is given by Boyd *et al.* (1947):

$$\ln(1 - F) = -Rt \dots \dots \dots (4)$$

where $R = \frac{3D^l}{r_0\Delta r_0\kappa}$. D^l is the surface (film) diffusion coefficient, r_0 the average adsorbate particle radius, Δr_0 the thickness of the film, κ the adsorbent distribution coefficient between the film and the solution. Figs. 3 and 4 show plot of $\ln(1-F)$ against time. When the straight line resulting from these plot of $\ln(1 - F)$ against time passes through the origin, it would indicate that the surface diffusion is the rate determining step of the process.

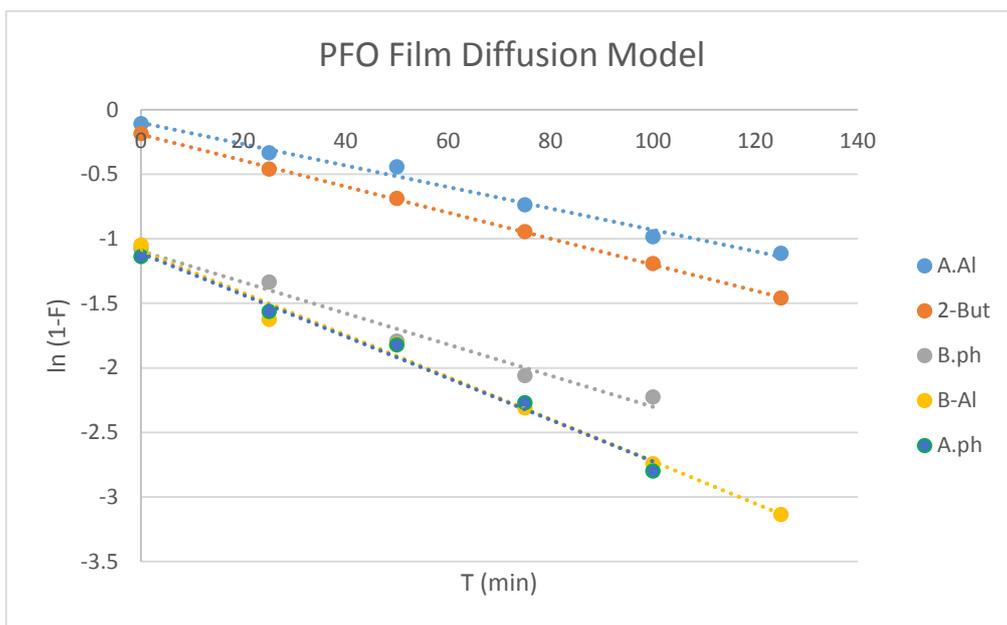


Fig. 3. Applying the Boyd surface diffusion model to the kinetic data generated by the PFO model.

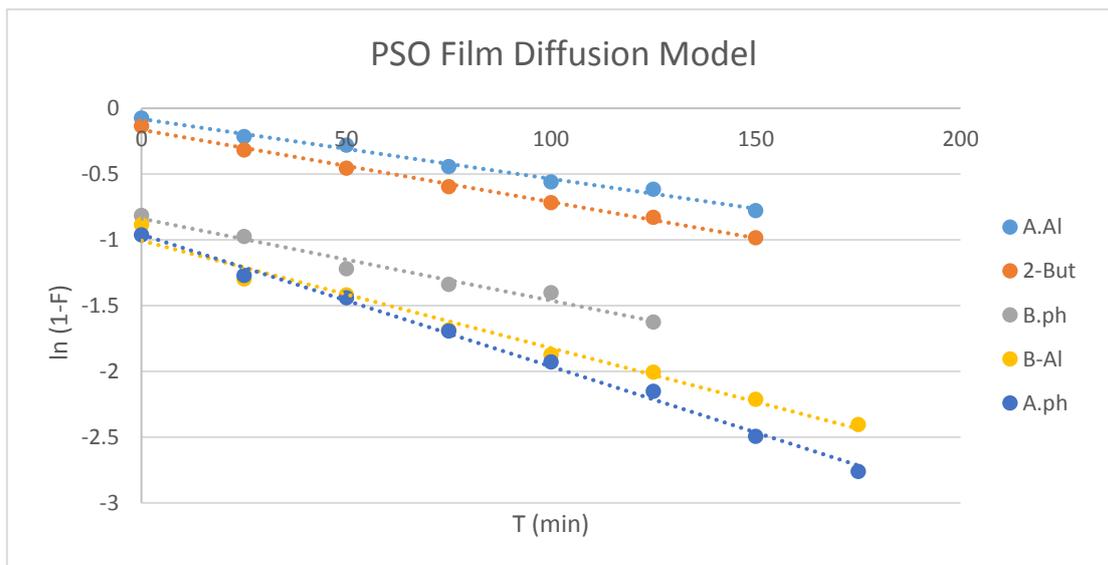


Fig. 4. Application of Boyd's surface diffusion model to the resulting kinetic data from PSO model.

As shown in these Figs., despite the good linear behavior, the values of the intersection points indicate that the surface diffusion process was not the rate determining step of the process for B.ph, B-Al and A.ph, while for A. Al and 2-But it is very likely that the surface diffusion process is the step determining the rate of adsorption. This is indicated by intersection points very close to the origin point and for both PFO and PSO kinetic models.

For porous diffusion, the following equation was developed by Boyd *et al.* (1947):

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-D^i \pi^2 n^2 t}{r_0^2}\right) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt) \dots \dots (5)$$

where, n is a positive integer, D^i is the diffusion coefficient within the pores (intraparticle diffusion coefficient). It is a common practice to use approximation when dealing with this equation depending upon the stage that is reached by the adsorption process where equation (5) is replaced by expressions 6 and 7 that are used in accordance with F values (Tsibranska & Hristova 2011; El-Khaiary & Malash 2011)

$$Bt = \frac{-\pi^2}{6} - \ln(1 - F) \text{ for } F > 0.85 \dots \dots (6)$$

$$Bt = \pi \left(1 - \sqrt{1 - \frac{\pi}{3} F}\right)^2 \text{ for } F < 0.85 \dots \dots (7)$$

where B is a constant termed Boyd number (Yoro *et al.* 2020). For $F > 0.85$, B is obtained by plotting $\frac{-\pi^2}{6} - \ln(1 - F)$ against time, while for $F < 0.85$ it is obtained from the plot of $\pi \left(1 - \sqrt{1 - \frac{\pi}{3} F}\right)^2$ versus time.

When porous diffusion is the rate-limiting step, the plot must be linear, passing through the origin in both cases of F values, the slope value of which is the constant B (Boyd number). A general trend was observed upon applying the above plots to the results obtained from the PFO and PSO models; where in the case of $F < 0.85$ the points of intersection are closer to the origin and have greater linear correlation than the case of $F > 0.85$ in both kinetic models (Table 6).

Table 6. Linear representation constants of Boyd's equation with correlation coefficient according to equations 5 and 6 for cases of Q_e computed from PFO and PSO models.

From PFO Q_e	A.Al	2-But	B.ph	B-Al	A.ph
slope	0.0055	0.0067	0.0131	0.0180	0.0175
F<0.85 intercept	-0.1166	-0.1182	-0.0666	0.0851	0.1105
r^2	0.9645	0.9772	0.9910	0.9788	0.9777
slope		0.0018	0.0451	0.0238	0.0254
F>0.85 intercept		1.3643	-4.7179	-0.6847	-0.8022
r^2		0.3780	0.9471	0.9701	0.9954
From PSO Q_e	A.Al	2-But	B.ph	B-Al	A.ph
slope	0.0017	0.0025	0.0062	0.0115	0.0113
F<0.85 intercept	-0.0202	-0.0038	0.0395	0.1058	0.1258
r^2	0.9647	0.9571	0.9929	0.9773	0.9749
slope			0.0000	0.0076	0.0055
F>0.85 intercept			1.4329	0.4163	0.9319
r^2			0.0000	0.9885	0.8977

Boyd's model of porous diffusion was more compatible when using the value of Q_e computed on the basis of the non-linear PSO model, as previously noted that the non-linear PSO model gave the possibility for the adsorption process to run over a period of time longer than that apparently estimated. Thus, this made it more consistent with Boyd's model, because the extension of the adsorption process over long period of time came in conjunction with

a large Q_e value. It leads to an increased number of experimental points that fulfill the condition $F < 0.85$, which is the region most responsive to Boyd's equation. The rate law, as we have previously noted, which is based on considering the surface activity as well as the activity of the adsorbate material in the adsorption process, is more consistent with the mathematical models of diffusion equations. Upon the determination of the constant B for the different cases of F and in both kinetic models and over the experimental points included in this study, it was found that in the cases of A.Al and 2-But the numerical value of the constant was somewhat more stable. The experimental points related to A.Al fall in the region of $F < 0.85$, which could be the reason behind the described stability. In the case of 2-But, for Q_e values calculated according to PSO model, the experimental points fall in the region of $F < 0.85$. For Q_e values obtained according to PFO model, the experimental points fall in both $F < 0.85$ and $F > 0.85$ ranges. These findings indicate that the kinetics of the adsorption process of A.Al and 2-But is consistent with the diffusive model derived by Boyd, whether for surface diffusion processes or for the pore diffusion process, especially in conjunction with the process constants determined according to the PSO model. These findings also indicate that for the adsorption of A.Al and 2-But, the surface diffusion process is equivalent to the porous diffusion process. This would further suggest that the thickness of the surface diffusion membrane Δr_0 along the radius of the adsorbate particle, are equal, $\Delta r_0 = r_0$ and thus the surface diffusion coefficient can not be distinguished from the coefficient of pore diffusion. The porous diffusion process for the compounds B.ph, A.ph and B.AL was apparently not compatible with Boyd's porous diffusion model. This was indicated by:

1. The large difference and instability of the values of the constant B determined according to the condition $F < 0.85$ and $F > 0.85$ (Figs. 5 and 6).

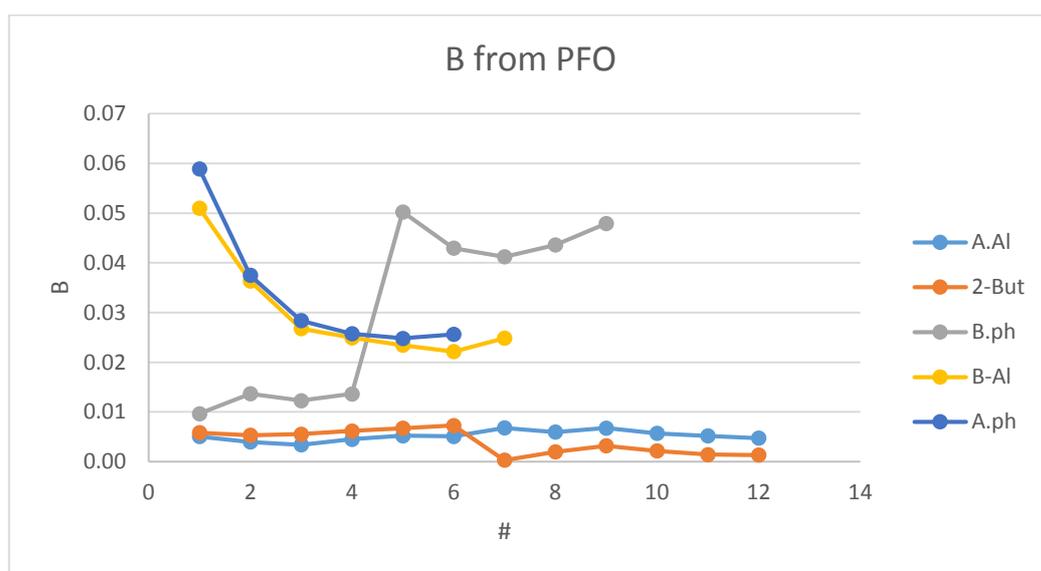


Fig. 5. The change in the value of the computed constant B from the linear representation of the inequalities of Boyd's equation for each experimental point. Some compounds have fewer experimental points due to $F \rightarrow 1$ at $Q(t) \rightarrow Q_e$ for Q_e values that are dependent upon PFO.

2. The linear representation of the inequality produced upon applying relations 6 and 7 were not passing through the origin as it can be seen from the intersection values presented in Table 6. The apparent incompatibility of the adsorption behavior of these three aromatic carbonyls with Boyd's porous diffusion model could be either in surface or in porous diffusion where the kinetics of diffusion are more complex. This adsorption behavior might be arose due to the fractal nature of the diffusion process where the value of the diffusion coefficient changes in a manner fractal with process flow (Balsamo & Montagnaro 2015). On the other hand, the kinetic of adsorption process for these compounds might not comprise the diffusion element. The large size of the aromatic carbonyl molecules, in comparison with A.AL and 2-But molecules, might obstructed them from penetrating into the pores of the surface particles. This obstruction led to low level of porous diffusion. Given surface diffusion, the kinetics of the process could have occurred as a result of direct adhesion of the adsorbate molecule onto the active site on the adsorbent's surface in such a manner that this adhesion is simultaneous and of a non-diffusive nature (localized). So that, there is no concentration gradient in the Δr_0 region, which is in accordance with Boyd's

surface diffusion hypothesis. According to aforementioned statements, it can be assumed that the determined B values for A.Al and 2-But can be used to compute the diffusion coefficients for both surface and porous diffusion of these two compounds into Porcelanite rocks, that is when the particle size distribution or the average diameters of the adsorbate particles are available.

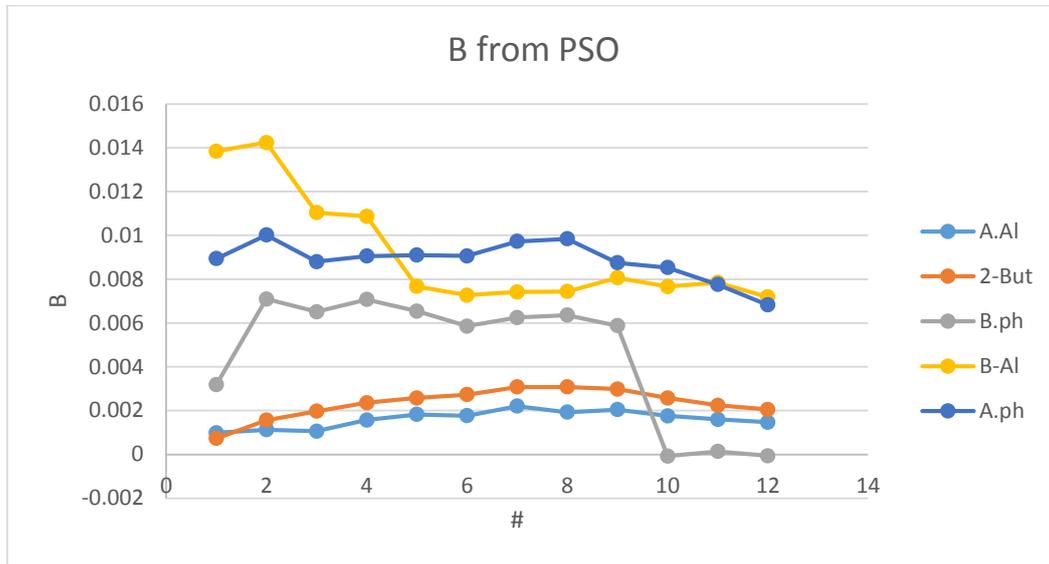


Fig. 6. The change in the value of the computed constant B from the linear representation of the inequalities of Boyd's equation for each experimental point. Some compounds have fewer experimental points because of $F \rightarrow 1$ at $Q(t) \rightarrow Q_e$ for Q_e values that are dependent upon PFO.

Table 7. Average of the constant B values over the experimental points obtained for Boyd's inequalities based on Q_e values calculated from the PFO and PSO kinematics.

	A.Al	2-But	B.ph	B-Al	A.ph
PFO \bar{B}	0.0052	0.0039	0.0306	0.0299	0.0335
PFO σ	0.0010	0.0023	0.0166	0.0096	0.0122
PSO \bar{B}	0.0016	0.0023	0.0046	0.0092	0.0089
PSO σ	0.0004	0.0007	0.0028	0.0025	0.0009

Weber-Morris diffusion model

Basically Weber-Morris model was used to describe the intraparticle diffusion of the solute in conditions of good agitation that insures reducing the contribution of the surface diffusion to the minimum (Weber & Morris 1963) otherwise, the plotting of $Q(t)$ vs. \sqrt{t} results into curves with intercept away from the origin, and hence the intraparticle diffusion will not be a rate limiting step of the adsorption process, while the contribution of the surface or film diffusion will be appreciable. Weber-Morris model was modified to include the effects of surface processes by inserting a constant. Moreover, segmenting the data points over sets each one of them describe the pore diffusion process depending on the pore type (Ofomaja 2008; Khaiary & Malash 2011; Schwaab *et al.* 2017). Experimental data were treated according to the modified Weber-Morris model given by the equation 8:

$$Q(t) = C + k_{ip}\sqrt{t} \dots \dots \dots (8)$$

where C represents the intersection value, and k_{ip} represents a constant that includes the diffusion coefficient of the adsorbate in the pores of the adsorbent. The results are presented in Fig. 7. The findings suggest that the diffusion process goes through three basic stages. The first stage is defined by the intersection values of the plots (Fig. 7). In the cases of A.Al and 2-But, the negative intercept values indicate that the membrane surrounding the adsorbent particles acts as a barrier, which leads to a delay in the adsorption process (Obradovic 2020). The amount of this delay can be obtained from the value of the intersection. It was 12.1 minutes in the case of A.Al and 5.23 minutes in that of 2-But. The intercept values in the cases of B.ph, A.ph and B.Al were positive. Positive intercept values indicate a very fast adsorption process. So that, the adsorbent seems to have contained an amount

of the adsorbate substance before the adsorption process started. This result is consistent with previously statements which exhibit that employing Boyd's diffusion model failed to explain the adsorption process data of the aromatic carbonyls.

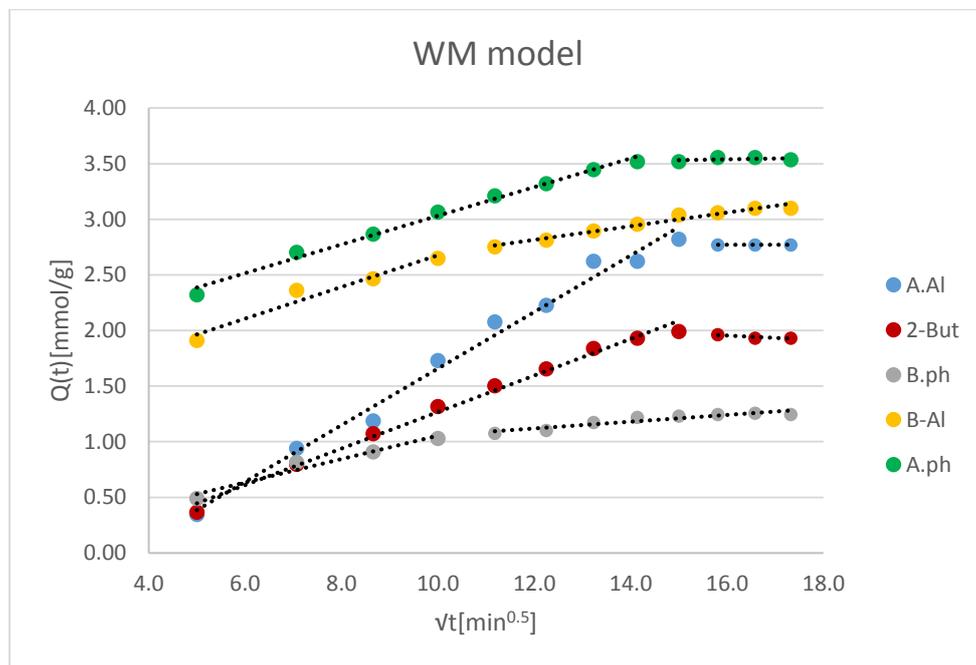


Fig. 7. Modified Weber-Morris model plots for the obtained kinematic data.

This failure can be attributed to the occurrence of adsorption process in a non-diffusive manner. It was more similar to adhesion process. The second stage refers to the normal diffusion behavior of the adsorption process until approaching equilibrium state. In the case of A.Al and 2-But, this stage extended until the 225th minute, while in those of B.ph and B.Al, it extended until the 100th minute. The second stage extended to 200th minute in that of A.ph. As for the third stage, it is represented by the final diffusion processes close to the equilibrium state, and as expected, in this stage the plots lines become less sloped and closer to a horizontal position.

CONCLUSION

The study presented in this work dealt with kinetics of adsorption of some organic carbonyl compound onto Iraqi porcelanite from their aqueous solutions. The obtained data were treated by a non-linear PFO and non-linear PSO methods. According to this treatment, the findings indicate that equilibrium time extended for a longer period in comparison to that observed. This might lead, as a consequence, to an absorbed amount higher than that recorded experimentally. This observation can be utilized by further future works to determine the suitable kinetic model to be applied to a practical data. In the present study, PSO was found to be the most suitable model to be applied. Studying the kinetic parameters by QSAR method showed enhancement effect on molar polarizability factor while the hydrophobicity and molar volume factors have a demotion effects. Boyd's model for surface diffusion and intraparticle diffusion was used for modeling kinetic data. The results revealed that A.Al and 2-But obey both kinds of diffusion indicating that the thickness of film diffusion layer is equal to adsorbate particle radius. For the other carbonyl compounds, our findings indicate that they have a good linear behavior according to Boyd's film diffusion model and with a significant intercept values. However, they didn't obey Boyd's pore diffusion model. Treatment of the same data with Weber-Morris diffusion model gave a more clear perspective about diffusion processes. In the cases of A.Al and 2-But the film boundary act to delay the process, so the film(surface) diffusion is more important than intraparticle diffusion in deciding the rate determining step. In the cases of A.ph, B.Al and B.ph, the initial step of adsorption was rapid and has a non-diffusible (localized) nature which is in agreement with results obtained in this work suggesting that these compounds did not obey Boyd's model. However, their behavior agrees with PFO and PSO treatments which indicate that these compounds are faster in reaching the equilibrium state.

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