

nisms that may be controlled by either pore or film diffusion and mass action [16], [27], [49]. In many adsorption processes, the adsorbate species may most probably be transported from the bulk of the solution into the solid phase through intra-particle diffusion/transport [27], [49]. Accordingly, the intra-particle (Weber and Morris) diffusion model was examined as per the following equation [12]:

$$q_t = k_i t^{0.5} + I \dots \dots \dots (12)$$

where q_t is the fraction of pollutant uptake (mg/g) at time t , k_i is the intra-particle-diffusion rate constant (mg/g min^{0.5}) and I is the intercept (mg/g). A plot of q_t vs. $t^{0.5}$ provided the values for k_i and intercept I that are listed in Table 4. In general, the value of the intercept provides some information about the thickness of the boundary layer and the larger the intercept the greater the boundary effect [35]. Overall, for all plots drawn, no zero intercept was obtained which may be indicative of some degree of boundary layer control and that may be operating simultaneously with other kinetic models to control the rate of adsorption [12], [27]. As well, it was observed that the correlation coefficients (R^2) obtained for the intraparticle diffusion model for both materials were more 0.810, which reflects that surface adsorption and intraparticle diffusion were concurrently operating during the adsorption process [12]. However, the effect of intraparticle diffusion upon TOC sorption onto Na-B was more as the temperature increased which indicates the fact that kinetically energetic molecules were able to be adsorbed onto it.

On the other hand, it was observed that the plot for q_t vs. $t^{0.5}$ for Na-B was curved initially which was followed by a linear portion. This noted curvature in the shape of the plot at a small time limit was reported to be due to mass transfer resistance and bulk diffusion while the linear portion may be attributed to intra-particle /pore diffusion [12], [27]. In order to assess the effect of pore diffusion during the process of TOC sorption onto SDS-B and Na-B, the Bangham's equation applied was [50]:

$$\log \log [C_i / (C_i - q_t m)] = \log [k_0 m / 2.303 V] \dots \dots \dots (13)$$

where C_s the weight of adsorbent used per liter of solution (mg/L), V (mL) is volume of solution, m (g/L) is the weight of adsorbent per liter of solution, q_t (mg/g) is the amount of adsorbate retained at time t and α (<1) and k_0 , are constants. $\log [C_i / (C_i - M q_t)]$ was plotted against $\log t$ and the plots obtained were not linear for both SDS-B and Na-B. This may indicate that the adsorption kinetics was not limited only by pore diffusion [50]. The values of k_0 and σ along with the correlation coefficient are presented in Table 4. According to the obtained correlation coefficients (R^2) for TOC adsorption onto Na-B, it is clear that both film and pore diffusion did contribute significantly to the different stages of the sorption mechanism.

TABLE 4
KINETIC PARAMETERS CALCULATED FOR THE REDUCTION OF TOC USING NA-B AND SDS-B AT DIFFERENT TEMPERATURES (°K), WHERE R^2 IS THE CORRELATION COEFFICIENT

Adsorbent	Temp (°K)	Pseudo-first-order			Pseudo-second-order			Intra-particle Diffusion			Bangham model		
		K_i (min ⁻¹) x10 ²	q_e (mg/g)	R^2	K_2 (g mg ⁻² min ⁻¹) x 10 ³	q_e (mg/g)	R^2	K_d (mg g ⁻¹ min ^{0.5}) x10 ³	I (mg/g)	R^2	k_0	α	R^2
SDS-B	298	3.616	8.097	0.8551	18.609	2.029	0.9997	17.40	1.9154	0.8488	473.07	0.0795	0.6864
	313	3.616	14.976	0.8558	9.727	1.970	0.9990	32.30	1.7587	0.8495	352.80	0.1007	0.6928
	323	3.316	14.827	0.8539	9.590	1.969	0.9989	32.00	1.7577	0.8325	352.55	0.0996	0.6728
	333	2.856	13.925	0.9135	9.946	1.962	0.9989	30.30	1.7599	0.8175	354.92	0.0936	0.6568
Na-B	298	11.40	2.580	0.9702	98.56	3.71 x10 ⁻²	0.9997	2.50	1.86	0.8720	1.67	0.2412	0.8674
	313	7.001	2.240	0.9750	42.55	3.53x10 ⁻²	0.9995	3.40	7.80	0.8749	7.31x10 ³	0.4727	0.8395
	323	9.995	3.853	0.9469	22.79	3.44x10 ⁻²	0.9973	3.70	2.20	0.9380	3.82x10 ³	0.6384	0.8851
	333	6.149	3.149	0.9317	12.22	3.67x10 ⁻²	0.9815	3.80	-1.10	0.9896	2.52x10 ³	0.7385	0.9380

4 CONCLUSION

In the current work, the adsorption of TOC from liquid solutions onto Na-bentonite and SDS-bentonite was investigated. The results showed that the experimental data was well represented by the second order kinetic model for both SDS-bentonite and Na-bentonite. As well, the data revealed that the process did involve some intraparticle diffusion for SBS-B. However, for NA-B, the results indicated that both intraparticle and pore diffusion significantly contributed or were the rate controlling steps of the overall adsorption process specifically at higher temperatures. The equilibrium data for both SDS-bentonite and Na-B were better fitted to Freundlich model. The apparent activation energies calculated for this process were -49.06 kJ/mol and -22.41 kJ/mol for Na-bentonite and SDS-bentonite, respectively. Thermodynamically the process was exothermic and spontaneous in the forward direction (irreversible) for SDS-bentonite while it was spontaneous in the backward direction (reversible) for Na-bentonite. The results also indicated a higher TOC removal using modified SDS-bentonite was more favored over Na-B due to its organophilic behavior after modification and smaller particle size.

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