Research Article

Isothermal and Kinetic Study of the Adsorption of Tetracycline Hydrochloride and Sulphamethoxazole by Bottom Ash and Alkali treated Bottom Ash

Dr. Lisha Kurup*

ABSTRACT

The two forms of Bottom Ash used for the adsorption of Tetracycline Hydrochloride and Sulphamethoxazole are Bottom Ash (BA) activated at 600 °C and activated (at 600 °C) Alkali treated Bottom Ash (ABA). Langmuir isotherm shows greater sorption capacity of ABA for Tetracycline Hydrochloride and Sulphamethoxazole than Bottom Ash. The thermodynamic parameters evaluated show that the adsorption of Tetracycline Hydrochloride on the two adsorbents is endothermic in nature whereas adsorption of Sulphamethoxazole shows exothermic nature. Dubinin Radushkevich isotherm was used to estimate sorption energy. Kinetic studies reveal that the processes in all the cases follow Ho Mckay's pseudo second order reaction. The studies of mass transfer coefficient for Tetracycline Hydrochloride and Sulphamethoxazole adsorption over ABA was higher than BA which suggests that ion-exchange reaction occurs more on ABA.

Key-words: Tetracycline Hydrochloride, Sulphamethoxazole, Adsorption, Bottom Ash, Adsorption Isotherm, Kinetics.

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1. Introduction

The presence of pharmaceuticals in our ecosystem is the result of increasing impact of human activities. Their discharge into water bodies adversely affects aquatic organisms\(^1\). In recent studies conducted in 11 countries, U.S. detected more than 80 pharmaceuticals and metabolites up to the \(\mu\)g/L level in sewage, surface, and ground water\(^2\).

Constant exposure to these drugs in low concentrations may not give rise to instant effects but will show its perilous effects for long term\(^3,4\). The two classes of antibiotics which are extensively in use are Tetracyclines and Sulpha drugs\(^5-7\). Besides their usage in wide variety of infections we cannot let down their ill-effects. These drugs have a long half-life thus they do not undergo complete degradation and leave their residue behind which may act as the precursor of allergic reactions\(^8-10\). In 1986, Sweden banned all the growth promoting antibiotics, following which European Union concerned with the emerging consequences of human and animal health also banned these drugs\(^11,12\).

Thus, to protect our biological system from the wrath of these drugs by their economically effective removal from industrial discharges is the prime concern of this research work.

Adsorption is a very effective and economical technique which has proven its versatility by removing not only the organic but also the inorganic compounds from water. The present work was undertaken to explore the feasibility of Bottom Ash (BA), a thermal power plant waste and Alkali treated Bottom Ash (ABA) for the removal of Tetracycline Hydrochloride and Sulphamethoxazole from water. Here Freundlich, Langmuir and Dubinin Radushkevich Isotherms and Kinetic parameters have been studied.

2. Materials and Methods:

Tetracycline Hydrochloride or 4-(Dimethylamino)-1, 4, 4a, 5, 5a, 6, 11, 12a-octahydro-3, 6, 10, 12, 12a-pentahydroxy-6-methyl-1,11-dioxo-2-naphthacenecarboxamidonitric acid with the molecular formula C\(_{22}\)H\(_{24}\)N\(_2\)O\(_8\).HCl and CAS No.64-75-5, was obtained from M/s HiMedia. While Sulphamethoxazole or 4-amino-N-(5-methylisoxazol-3-yl)-benzenesulfonamide with the molecular formula C\(_{10}\)H\(_{11}\)N\(_3\)O\(_3\)S and CAS No. 723-46-6 was obtained from Sigma-Aldrich. All the other reagents used were of A.R. grade. The adsorbent BA was procured from Bharat Heavy Electricals Limited, Bhopal. The instruments used were pH meter model number LI 120 ELICO, incubator cum shaker of model IS-971R was used and absorbance measurements were carried out on UV/Vis spectrometer (M/s Perkin Elmer, Lambda 25). For IR studies FTIR spectrometer (M/s Perkin Elmer, Spectrum BX) was used. For SEM, JEOL/E0, version 1.0 and for XRD measurements Bruker D8 Advance X-ray diffractometer was used.

2.1 Preparation of Adsorbents:

BA was washed with water and dried. The adsorbent was then treated with Hydrogen Peroxide (30%) till effervescence seized, subsequently it was left undisturbed for 24 hours. It was given a thorough washing with doubly distilled water and was then air dried and kept in an oven at 100\(^\circ\)C for 1 hour. Dried BA was then activated at 600\(^\circ\)C for 15 minutes. A portion of the above activated BA was sieved through 150, 170 and 200 BSS Mesh sieves and was kept in a desiccators for subsequent use. The other portion was treated with 2N Sodium Hydroxide for thirty days and was filtered simultaneously with thorough washing with distilled water.

2.2 Adsorption and Kinetic Studies:

Analysis were carried out at different conditions of pH, concentration, time, amount of adsorbent, temperature and sieve size to check the propensity of adsorption process. After undergoing these experimental procedures, a concentration of \(2 \times 10^{-4}\)M, sieve size of 200 BSS Mesh and amount of 0.1 g were chosen for subsequent studies. For the analysis, 25mL of antibiotic solution of known concentration

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and pH was poured into 100 mL conical flasks, having known amounts of adsorbent. The mixture was shaken at a particular temperature for 24 hours for saturation. Thereafter, supernatant liquid was filtered through Whatmann Filter Paper No.42 and the amount of antibiotic adsorbed was determined spectrophotometrically at the $\lambda_{\text{max}}$ 275 nm and 265 nm respectively for Tetracycline Hydrochloride and Sulphamethoxazole.

Batch technique was also employed to monitor the kinetics of the adsorption. In a stoppered airtight 100 mL conical flask, 25 mL of antibiotic solution of known concentration was taken. A known amount of adsorbent was added and the flask was agitated by mechanical shaker maintained at desired temperature. After a definite time interval, solution of the flasks was filtered and filtrate thus obtained was analyzed spectrophotometrically to determine the uptake of the drug.

3. Results and discussion
3.1. Characterization of Adsorbents:

3.1.1 Physical Characterization of Adsorbent:
Experiments were carried out for determining the cation exchange capacity (CEC), zero point charge (ZPC) and percentage porosity of the two adsorbents. The porosity data obtained for BA (37.135%) was found to be more than that of ABA (14.462%). This can be attributed from the fact that when BA is treated with alkali, the ions must have occupied the surface and the pores of BA which decreases the porosity of ABA. The CEC of BA and ABA was found to be 1.258 meq/g and 3.773 meq/g respectively while ZPC was calculated as 5.21 and 7.50 respectively. The increase in CEC of ABA may be due to increase in ionic concentration over the surface of ABA.

3.1.2. Infrared Spectroscopy:
The IR spectrum of activated BA exhibited adsorption bands in the region 3466 and 1638 cm$^{-1}$. The peak at 1638 cm$^{-1}$ shows the presence of carbonates. On the other hand ABA IR-spectra shows the peaks at the same region but it was seen that the peaks were much broader and shifted towards lower frequency exhibiting the occurrence of reaction between BA and alkali which has resulted into new product. When these adsorbents were treated with Tetracycline Hydrochloride the bands becomes sharper and shifts towards lower frequency. Thus, these displacements again confirm the reaction between adsorbents and adsorbate (Figure S1). The same feature was obtained with Sulphamethoxazole adsorbed BA and ABA (Figure not given).
3.1.3. X-Ray Diffraction and Scanning Electron Microscopy Analysis:
The peaks at 2θ values of 26.498 and 36.481 of X-Ray Diffraction pattern in Figure S2 clearly shows the presence of Quartz (SiO₂) and Mullite (Al₆Si₂O₁₃) respectively in the activated BA. While a decrease in the intensity of these peaks are observed in case of ABA. Moreover, the peaks at 2θ values of 33.174 and 60.094 are seen in the XRD of ABA which reveals the appearance of Zeolite (Na₆[AlSiO₄]₆.4H₂O) confirming the transformation in BA.

The SEM images (Figure1a) of BA clearly reveal the presence of Quartz and Alumina whereas white aggregates can be seen in case of ABA (Figure1b) which shows the formation of Zeolite.
3.2. Effect of pH:

The Tetracycline Hydrochloride exhibits three acidity constants. In the pH less than 3.1 the compound exist in its protonated state whereas in the pH range of 4.2 – 7.2 it undergoes deprotonation and exhibits zwitter ionic state and at a pH of 9.2 about 80% of molecules are present as anionic species. In the solution of pH 5.0 the drug chiefly shows neutral nature. On the other hand, it may be present in either zwitter ion or a cation in the pH of 4 and as an anion in the solution of pH 6 – 7. The pH_{zpc} of BA and ABA lies at pH 5.2 and pH 7.5 respectively and exhibits positive nature below pH_{zpc}. BA and ABA shows maximum removal of 69.0% and 89.5% respectively at a pH of 4.0 respectively. This can be attributed by the fact that adsorption on BA and ABA takes place through ion exchange.

On the other hand, the pH study of Sulphamethoxazole showed an increase in adsorption till pH 4 and 5 respectively for BA and ABA and then decreases. This can be attributed to the fact that the dissociation constant of Sulphamethoxazole is 1.8 and 5.6 due to which it exist in protonated state from pH1.8 – 5.6 and after this deprotonation starts and Sulphamethoxazole becomes negatively charged. Thus, ion exchange is more at above mentioned pH and as the pH becomes higher than pH_{zpc} the adsorption decreases.

3.3. Adsorption Isotherm:

The sorption experiments were carried out in 100 mL conical flasks for different concentrations ranging from 5 × 10^{-5} to 2 × 10^{-4} M at different temperatures of 27°C and 40°C. The equilibrium data analyzed from these investigations were used to obtain different adsorption isotherms like Langmuir, Freundlich and Dubinin-Radushkevich isotherms.

3.3.1. Langmuir adsorption isotherm:

Langmuir sorption isotherm hypothesizes the monolayer adsorption on the surface containing finite adsorption sites. It can be used to deduce the sorption capacity of the adsorbent. The equation can be shown as:

\[
\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bC_eQ_o} \quad \ldots 1
\]

where, \(C_e\) is the molar concentration in solution at equilibrium, \(Q_o\) is number of moles of solute adsorbed per unit weight of adsorbent, \(q_e\) is the number of moles of solute adsorbed per unit weight at concentration \(C\) and \(b\) is Langmuir constant.

The graph plotted between \(1/C_e\) versus \(1/q_e\) in Figure S3 with Tetracycline Hydrochloride–Adsorbent System shows an increase in the value of sorption capacity \((Q^o)\) with the temperature.
exhibiting endothermic nature of the ongoing reaction, whereas reverse is seen with Sulphamethoxazole–Adsorbent System revealing the exothermic nature of the process (Figure S4). Moreover in both the systems ABA shows a higher sorption capacity than the activated BA which can be assumed to be due to the availability of more exchangeable sites than the other one. The data has been specified in Table 1. Langmuir adsorption isotherm was also used in estimating thermodynamic parameters (equation 2, 3, and 4) which has been shown in Table 2. Negative values of $\Delta G^\circ$ and positive value of $\Delta H^\circ$ in case of Tetracycline Hydrochloride–Adsorbent System confirm the feasibility of process with rising temperature. On the other hand negative value of $\Delta H^\circ$ in case of Sulphamethoxazole–Adsorbent System validates the exothermic nature of this process.

$$\Delta G^\circ = -RT \ln b \quad ...2$$

$$\Delta H^\circ = -R \frac{T_2 \times T_1}{T_2 - T_1} \ln \frac{b_2}{b_1} \quad ...3$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \quad ...4$$

where, $\Delta G^\circ$ is Gibb’s free energy, $\Delta S^\circ$ is change in entropy and $\Delta H^\circ$ is change in enthalpy, R is the gas constant and $b$, $b_1$, $b_2$ are the equilibrium constants at different temperatures and obtained from the slopes of Langmuir adsorption isotherms at different temperatures.

**Table 1** Freundlich, Langmuir and Dubinin Radushkevich Isotherm Constants for removal of Tetracycline Hydrochloride (TH) and Sulphamethoxazole (SM) using Bottom Ash (BA) and Alkali treated Bottom Ash (ABA) at different temperatures.

<table>
<thead>
<tr>
<th>Antibiotic</th>
<th>Adsorbent</th>
<th>Langmuir Isotherm</th>
<th>Freundlich Isotherm</th>
<th>D-R Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$Q^\circ \times 10^{-2}$</td>
<td>$b \times 10^{3}$</td>
<td>$K_F$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(mol g$^{-1}$)</td>
<td>(L mol$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>TH</td>
<td>BA</td>
<td>0.16</td>
<td>0.23</td>
<td>52.30</td>
</tr>
<tr>
<td></td>
<td>ABA</td>
<td>0.21</td>
<td>0.31</td>
<td>139.9</td>
</tr>
<tr>
<td>SM</td>
<td>BA</td>
<td>0.06</td>
<td>0.04</td>
<td>41.76</td>
</tr>
<tr>
<td></td>
<td>ABA</td>
<td>0.10</td>
<td>0.06</td>
<td>129.9</td>
</tr>
</tbody>
</table>

[Adsorbent Dose = 0.1 g, Particle Size ≤200 BSS Mesh, pH = 4.0]

**Table 2** Thermodynamic Parameters for the uptake of Tetracycline Hydrochloride and Sulphamethoxazole by Bottom Ash and Alkali treated Bottom Ash

<table>
<thead>
<tr>
<th>Antibiotic</th>
<th>Adsorbent</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (JK$^{-1}$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetracycline Hydrochloride</td>
<td>BA</td>
<td>27.630</td>
<td>2.558</td>
<td>98.493</td>
</tr>
<tr>
<td></td>
<td>ABA</td>
<td>29.752</td>
<td>20.370</td>
<td>163.529</td>
</tr>
<tr>
<td>Sulphamethoxazole</td>
<td>BA</td>
<td>27.381</td>
<td>-12.379</td>
<td>48.946</td>
</tr>
<tr>
<td></td>
<td>ABA</td>
<td>31.290</td>
<td>-59.349</td>
<td>-91.546</td>
</tr>
</tbody>
</table>
3.3.2. Freundlich Adsorption Isotherm:
The Freundlich isotherm, presumes that the surface has different sites with different adsorption energies. This assumption was used to obtain sorption equilibrium data. Freundlich model can be illustrated as:

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \quad \ldots 5 \]

where, \( C_e \) is the molar concentration in solution at equilibrium, \( q_e \) is the number of moles of solute adsorbed per unit weight at concentration \( C \) and \( K_f \) and \( n \) are Freundlich constants. The values of Freundlich constants \( K_f \) and \( n \) derived respectively from the intercept and slope of the curve plotted between \( \log C_e \) and \( \log q_e \) for both the systems i.e. Tetracycline Hydrochloride (Figure S5) and Sulphamethoxazole (Figure not shown) are summarized in Table1. The R-squared value obtained from the plots of Freundlich adsorption isotherms was greater than that obtained in Langmuir plots. This shows that adsorbents are composed of heterogeneous adsorption surface with different classes of adsorption sites.
3.3.3. Dubinin-Radushkevich isotherm (D-R Isotherm):
D-R Isotherm\textsuperscript{13} was used to interpret whether the sorption mechanism is physisorption or chemisorptions. The D-R model is expressed in the following linear form:

$$\ln q_e = \ln X_m - \beta \epsilon^2 \quad \ldots 6$$

where $q_e$ represents the amount of antibiotic adsorbed per unit weight of adsorbent, $X_m$ is the maximum sorption capacity, $\beta$ the activity coefficient related to mean sorption energy, and $\epsilon$ is the Polanyi potential, which is equal to

$$\epsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad \ldots 7$$

where, $C_e$ is the molar concentration in solution at equilibrium $R$ is the universal gas constant and $T$ is the temperature. The value of $\beta$ was evaluated from the slope of the graph plotted between $\ln q_e$ vs $\epsilon^2$ while the intercept capitate the sorption capacity $X_m$. The mean sorption energy ($E$) (Table 1) given by-

$$E = \frac{1}{\sqrt{-2\beta}} \quad \ldots 8$$

E is a significant parameter for distinguishing between physisorption and chemisorption, for heterogeneous surfaces of the adsorbent. If the value of $E$ comes in between 8 – 16 kJ/mol then the adsorption is explicated to proceed by ion-exchange mechanism\textsuperscript{14}. In the present work the value of sorption energy ($E$) comes in above range thereby revealing the process of adsorption of Tetracycline Hydrochloride and Sulphamethoxazole to be taking place on to the selected adsorbents by the mechanism of ion-exchange.

3.4. Kinetic Studies:
The first task in kinetic investigation is to measure the rates of reaction under various experimental conditions like different sieve size, amount of adsorbent, concentration, temperature and contact time. The values of half life period obtained at different concentrations and temperatures for both the adsorbents (Table 3) clearly portrays an increased adsorption at lower concentrations.

<table>
<thead>
<tr>
<th>Concentration (µM)</th>
<th>Tetracycline Hydrochloride</th>
<th>Sulphamethoxazole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t_{1/2}$ (BA) hr</td>
<td>$t_{1/2}$ (ABA) hr</td>
</tr>
<tr>
<td>27°C 40°C</td>
<td>27°C 40°C</td>
<td>27°C 40°C</td>
</tr>
<tr>
<td>90</td>
<td>7.309 4.424</td>
<td>2.025 1.383</td>
</tr>
<tr>
<td>100</td>
<td>8.005 4.919</td>
<td>2.668 1.808</td>
</tr>
<tr>
<td>200</td>
<td>10.292 8.005</td>
<td>2.968 1.947</td>
</tr>
</tbody>
</table>

The adsorption progression was also explored at different temperatures of 27°C and 40°C. In case of Tetracycline Hydrochloride (Figure S6) an increase in adsorption is noticed with the rise in temperature, which specifies the endothermic nature of the process, while adsorption of Sulphamethoxazole is more pronounced at lower temperature confirming the exothermic nature of the process. This may be assumed due to the increase in the rate of diffusion which leads to greater mass transfer of the solute from the solvent to the adsorbent with increasing temperature.

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For the study of contact time with both the adsorbents separate solutions of a particular concentration, pH and volume was taken and was fed with definite amount of adsorbent. For both the adsorbents the adsorption of Tetracycline Hydrochloride and Sulphamethoxazole, first increases with the time but attain saturation within 4–8 hours (Figure S6). The data evaluated from this study was then used for obtaining the rate constant, effective diffusion coefficient and mass transfer coefficient of adsorbate.

3.4.1. Pseudo-First-Order Equation:
Lagergren’s pseudo-first order equation was analyzed with the data obtained. The equation can be expressed as:

\[
\log(q_e - q_t) = \log q_e - \frac{kt}{2.303} \quad \ldots 9
\]

Where, \( q_e \) and \( q_t \) are the amount of drug adsorbed at equilibrium and at time ‘t’ respectively while \( k_{ad} \) (min\(^{-1}\)) is the rate constant of the pseudo-first order adsorption. Plots of \( \log(q_e - q_t) \) versus time in Figure 2 at different temperatures portrays the validity of pseudo-first order equation. The R-squared value obtained for both the adsorbents in both the systems was lower than the R-squared value obtained for pseudo second order equation. The values of rate constant have been discussed in Table 4.

3.4.2. Pseudo-Second-Order Equation:
The experimental data was further verified by subjecting it to Ho and Mckay’s pseudo-second-order adsorption\textsuperscript{15}. The simplest way to describe the kinetics of removal can be expressed as:

\[
\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad \ldots \quad 10
\]

\[
h = kq_e^2 \quad \ldots \quad 11
\]

where, \(q_e\) and \(q_t\) are the amount of drug adsorbed at equilibrium and at time ‘\(t\)’ respectively, \(k\) is the pseudo-second order rate constant and \(h\) is the initial sorption rate. The plot of \(t/q_t\) vs \(t\) gives a straight line. The value of rate of sorption, \(k\) was estimated (Table 4) from the slope and intercept of the plot which in turn was used to assess the initial sorption rate, \(h\). The curve (Figure 3) obtained in this case exhibits more conjunction with both the adsorbents which is revealed from the R-square value exhibited in the plot. This shows that the ongoing processes follow the pseudo second order rate equation.

**Table 4 Value of Rate Constant of Pseudo First Order and Pseudo Second Order Plots and Mass Transfer Coefficient (\(\beta_L\)) Values of Adsorption of Tetracycline Hydrochloride and Sulphamethoxazole at Different Temperatures.**

<table>
<thead>
<tr>
<th>Antibiotic</th>
<th>Adsorbent</th>
<th>Rate Constant (k)</th>
<th>(\beta_L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pseudo First Order (min(^{-1}))</td>
<td>Pseudo Second Order (L mol(^{-1}) min(^{-1}))</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27°C</td>
<td>40°C</td>
</tr>
<tr>
<td>Tetracycline Hydrochloride</td>
<td>BA</td>
<td>0.0051</td>
<td>0.0067</td>
</tr>
<tr>
<td></td>
<td>ABA</td>
<td>0.0046</td>
<td>0.0069</td>
</tr>
<tr>
<td>Sulphamethoxazole</td>
<td>BA</td>
<td>0.0064</td>
<td>0.0058</td>
</tr>
<tr>
<td></td>
<td>ABA</td>
<td>0.013</td>
<td>0.012</td>
</tr>
</tbody>
</table>

*Figure 3: Plot of Ho and McKay’s Pseudo Second Order Adsorption Reaction of adsorbents with Tetracycline Hydrochloride (TH) and Sulphamethoxazole (SM)*
3.4.3. Mass Transfer Study:

To evaluate the efficacy of the adsorbents for the treatment of Tetracycline Hydrochloride, the values of the surface mass transfer coefficient ($\beta_L$) were calculated by applying mathematical mass transfer model given by McKay et al\textsuperscript{16} using equation:

$$\ln\left(\frac{C_t}{C_o} - \frac{1}{1 + mk}\right) = \left(1 + \frac{mk}{\beta_L S_s}\right)t + \left(\frac{mk}{1 + mk}\right) \quad \text{... 12}$$

where, $C_o$ is initial concentration of adsorbate (mgL\textsuperscript{-1}), $C_t$ is concentration of adsorbate (mgL\textsuperscript{-1}) after time $t$, $m$ is mass of adsorbent per unit volume of particle free adsorbate solution (gL\textsuperscript{-1}), $k$ is Langmuir constant (Lg\textsuperscript{-1}) obtained by multiplying adsorption capacity, $Q_o$ and adsorption energy, $b$. $\beta_L$ is the mass transfer coefficient (cm.sec\textsuperscript{-1}) and $S_s$ the outer surface of the adsorbent per unit volume of particle-free slurry (cm\textsuperscript{-1}) the values of $m$ and $S_s$ are calculated using the following equations:

$$m = \frac{W}{V} \quad \text{... 13}$$

$$S_s = \frac{6m}{(1 - \varepsilon_P)d_P \rho_P} \quad \text{... 14}$$

where, $W$ is weight of adsorbent (g), $V$ is volume of particle free adsorbate solution (L), $d_P$ is particle diameter (cm), $\rho_P$ is density of adsorbent (g.cm\textsuperscript{-3}) and $\varepsilon_P$ is the porosity of the adsorbent particle.

The graph plotted between $\ln\left(\frac{C_t}{C_o} - \frac{1}{1 + mk}\right)$ versus time (Figure 4) gives a straight line which shows the rapid movement of Tetracycline Hydrochloride and Sulphamethoxazole from bulk to solid phase. Moreover the mass transfer coefficient (Table 4) of ABA is more than BA in both the cases therefore exhibiting greater adsorption efficiency of ABA to that of BA.

![Figure 4: Plot of time versus $\ln\left(C_t/C_o - (1/(1+mk))\right)$ for the Mass Transfer of Tetracycline Hydrochloride (TH) and Sulphamethoxazole (SM) into Bottom Ash (BA) and Alkali treated Bottom Ash (ABA) at Different Temperatures](image)

3.4.4. Rate expression and treatment of data:

For proper interpretation of experimental data and to analyze whether process takes place through film diffusion or particle diffusion the kinetic data was subjected to mathematical treatment suggested by Boyd et al\textsuperscript{17} and Reichenberg\textsuperscript{18}.

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The following expression was used to investigate the exact process involved in the present adsorption.

\[ F = 1 - \frac{6}{n^2} \sum_{1}^{\infty} \frac{n^2}{B_1} \exp(-n^2B_1) \quad ... 15 \]

where, \( n \) is Freundlich constant of the adsorbate and \( F \) is the fractional attainment of equilibrium at time ‘t’ which is obtained by using following equation

\[ F = \frac{Q_t}{Q_\infty} \quad ... 16 \]

where, \( Q_t \) and \( Q_\infty \) are amounts adsorbed after time \( t \) and after infinite time respectively. The curve obtained in \( B_t \) versus time graph for Tetracycline Hydrochloride adsorption on BA and ABA showed particle diffusion at lower as well as at higher concentration (Figure 5). The same trend was seen during the adsorption of Sulphamethoxazole over BA and ABA (Figure not shown). The slope obtained from the plot of \( B_t \) versus time was used to evaluate the effective diffusion coefficient of adsorbate in the adsorbent phase using following equation,

\[ B = \frac{n^2D_i}{r_o^2} = \text{Time Constant} \quad ... 17 \]

where, \( D_i \) is the effective diffusion coefficient of the adsorbate and \( r_o \) is the radius of adsorbent particles assumed to be spherical. \( D_i \) values obtained at different temperatures for both the adsorbate showed an increase with increasing temperature indicating thereby an increase in the mobility of the ions with increase in temperature. The intercepts obtained from these graphs were used to derive the value of pre exponential constant \( (D_o) \) analogous to the Arrhenius frequency factor, which was used to find out the value of activation energy \( E_a \) and entropy of activation \( \Delta S^\# \) using following equations:

\[ D_i = D_o \exp \left( -\frac{E_a}{RT} \right) \quad ... 18 \]

\[ D_o = \left( \frac{2.72d^2kT}{h} \right) \exp \left( \frac{\Delta S^\#}{R} \right) \quad ... 19 \]

Here \( d \) is the average distance between the two adsorption sites and has been taken as 5 Å for the particle sizes of the adsorbents chosen. The values of \( E_a, D_o \) and \( \Delta S^\# \) for the diffusion of Tetracycline Hydrochloride and Sulphamethoxazole are listed in Table 5.

**Table 5 Values of Effective Diffusion Coefficient (\( D_i \)), Activation Energy (\( E_a \)) and Entropy of Activation (\( \Delta S^\# \)) for the Diffusion of Tetracycline Hydrochloride and Sulphamethoxazole into Bottom Ash and Alkali treated Bottom Ash**

<table>
<thead>
<tr>
<th>Antibiotic</th>
<th>Adsorbent</th>
<th>( D_i ) (m^2/s)</th>
<th>( E_a ) (kJ mol^-1)</th>
<th>( -\Delta S^# ) (JK^-1 mol^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetracycline Hydrochloride</td>
<td>BA</td>
<td>( 7.131 \times 10^{-13} )</td>
<td>( 8.986 \times 10^{-13} )</td>
<td>( 61.185 )</td>
</tr>
<tr>
<td></td>
<td>ABA</td>
<td>( 8.843 \times 10^{-13} )</td>
<td>( 9.984 \times 10^{-13} )</td>
<td>( 59.152 )</td>
</tr>
<tr>
<td>Sulphamethoxazole</td>
<td>BA</td>
<td>( 7.845 \times 10^{-13} )</td>
<td>( 6.133 \times 10^{-13} )</td>
<td>( 55.081 )</td>
</tr>
<tr>
<td></td>
<td>ABA</td>
<td>( 1.184 \times 10^{-12} )</td>
<td>( 1.055 \times 10^{-12} )</td>
<td>( 54.963 )</td>
</tr>
</tbody>
</table>

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